BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1953

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$C_4H_{11}N$. 1) Diethylamine, reaction with 4-chloro-3-buten-2-one, 885; reaction with ethylene oxide to 2-(diethylamino)ethanol, 336; reaction with 2-methyl-1,5-hexadien-3-one, 5-methoxy-2-methyl-1-hexen-3-one, 1,5-hexadien-3-one, methoxy ketones, 290.

2) 1-Methylpropylamine, reductive amination product of 2-butanone, formation, properties, 83.

$C_4H_{12}Si$. Tetramethylsilane, preparation, properties, Raman spectra, 267.

4. III

$C_4H_4OF_6$. 2H-Hexafluoropropyl methyl ether, preparation, properties, 255.

$C_4H_4SF_6$. 2H-Hexafluoropropyl methyl sulfide, preparation, properties, 255.

$C_4H_4O_2F_4$. Methyl 2H-tetrafluoropropionate, preparation, properties, 259.

C_4H_5OCl. Methyl-β-chlorovinyl ketone, reaction with β-naphthol, 430.

$C_4H_6O_2Hg$. Mercuric acetate, reaction with menthyl and bornyl esters of cinnamic acid, 583.

$C_4H_7O_2Br$. Ethyl bromoacetate, reaction with mercury, 592.

$C_4H_7O_2I$. Ethyl iodoacetate, reaction with mercury, 594.

$C_4H_8OCl_2$. 1) Bis(2-chloroethyl)ether, preparation, 527.

2) "Chlorex," conversion to divinyl ether, 643.

$C_4H_8O_2Br_2$. Dioxan dibromide, reaction with 2-methylcyclohexanone, 793.

$C_4H_{10}OS$. 1-Ethoxyethanethiol, reaction with ethyl vinyl ether, 331.

$C_4H_{11}O_3P$. Diethyl hydrogen phosphite, reaction with aldehydes and ammonia, 770.

4. IV

$C_4H_3OF_5Br_2$. 2,3-Dibromopentafluoropropyl methyl ether, preparation, properties, 255.

$C_4H_7O_2HgI$. Ethyl iodomercuriacetate, preparation, properties, 594.

$C_4H_{10}O_2PCl$. Chloranhydride of diethylphosphorous acid, preparation, properties, 435.

$C_4H_{10}O_2SiCl_2$. Diethoxydichlorosilane, preparation, properties, 436.

$C_4H_{11}O_2PS$. Diethyl phosphite, reaction with sulfur, 153.

$C_4H_{11}O_2PS_2$. O,O-Diethyl hydrogen phosphorothiolothionate, preparation, properties, lead salt, titration, oxidation with iodine, 110.

$C_4H_{12}NPO_3$. Phosphonobetaine, preparation, reaction, with HI, 1001.

$C_4H_{12}O_4P_2S_4$. Disulfide obtained from O,O-dimethyl hydrogen phosphorothiolothionate, 111.

4. V

$C_4H_{10}O_2PSCl$. Diethyl phosphorochloridothionate, preparation, properties, 153.

$C_4H_{10}O_2PSNa$. 1) Sodium butyl thiophosphite (phosphothionate), preparation, 153.

2) Sodium O,O-diethyl phosphorothiite, preparation, reaction with sulfur ethyl iodide, ethyl chloride, benzyl chloride, 154.

$C_4H_{12}O_4P_2S_4Ni$. Nickel bis(O,O-dimethyl phosphorothiolothionate, preparation. 110.

Group C_5

5. I

C_5H_6. Cyclopentadiene, preparation by depolymerization of dicyclopentadiene, 101.

C_5H_8. Isoprene, properties, hydrogenation in presence of platinum, palladium and nickel, 601.

C_5H_{10}. 1) Cyclopentane, formation from carbon monoxide and hydrogen, 914; properties, catalytic reactions under a pressure of hydrogen at high temperature, hydrogenolysis, hydrogenosynthesis, 243.

2) 2-Methyl-2-butene, formation by hydrogenation of isoprene, 603.

3) 2-, and 3-methyl-1-butene, formation by hydrogenation of isoprene, 603.

C_5H_{12}. 1) 2-Methylbutane, formation from cyclopentane, 243; formation from hexane, heptane, 780.

2) Pentane, conversion into liquid hydrocarbons and gas at 250 - 360 atmospheres and 400 - 500°, cracking, destructive alkylation, isomerization, cyclization, polymerization, 237; formation from heptane, 781; formation from hexane, 780; n-, and iso-, formation from cyclopentane, 243.

3) Isopentane, formation by hydrogenation of isoprene, 603.

4) Tetramethylmethane, frequencies of C—H valency vibrations, 269.

5. II

C_5H_4O. 2-Cyclopenten-1-one, preparation, properties, ozonization, 796; condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone, and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone, 827.

$C_5H_4O_3$. Citraconic anhydride, condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone, 817.

C_5H_5N. Pyridine, reaction with dichloro (diallylamine) platinum, 210.

C_5H_6O. 2-Cyclopenten-1-one, condensation with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, 978.

$C_5H_6N_2$. 2-Aminopyridine, relative basicity of nitrogen atoms, absorption spectrum, 129; reaction with ethylene oxide, 133.

$C_5H_7Cl_3$. 1,1,5-Trichloropentene, formation, properties, 879.

C_5H_8O. 1) Cyclopentanone, properties, reductive amination, 81.

2) 2-Methoxy-1,3-butadiene, preparation, condensation with 2-methyl-2-cyclohexen-1-one, 74.

$C_5H_8Cl_2$. 1,1-Dichloropentene, preparation, properties, 880.

$C_5H_8Cl_4$. 1,1,1,5-Tetrachloropentane, removal of HCl from, 879.

$C_5H_8O_3$. Vinyl lactate, preparation, hydrolysis, properties, 499.

$C_5H_8O_4$. Glutaric acid, formation, 793.

$C_5H_9Cl_3$. Trichloropentane, splitting off HCl, 880.

$C_5H_{10}O$. 1) Propyl vinyl ether, properties, ionic polymerization of, 940.

2) n- and iso-Propyl vinyl ether, properties, reaction with 2-chloroethanol, 927.

3) Isopropyl vinyl ether, properties, ionic polymerization of, 940; properties, reaction with acetylenic alcohols to form acetals, 946.

4) 3-Pentanone, properties, reductive amination of, 81.

$C_5H_{11}N$. Piperidine, reaction with methoxy ketone to form amino ketone, 290; reaction with 4-chloro-3-buten-2-one, 885.

$C_5H_{13}N$. 1-Ethylpropylamine, reductive amination product of 3-pentanone, 82.

$C_5H_{14}Si$. Ethyltrimethylsilane, preparation, properties, Raman spectra, 267.

5. III

$C_5H_6OF_6$. Ethyl 2H-hexafluoropropyl ether, preparation. properties, 255.

$C_5H_6SF_6$. Ethyl 2H-hexafluoropropyl sulfide, preparation properties, 255.

$C_5H_6O_2F_4$. Ethyl 2H-tetrafluoropropionate, preparation, properties, 259.

$C_5H_9O_2Br$. Ethyl 2-bromopropionate, reaction with mercury, 592.

$C_5H_{10}O_2Cl_2$. 1) Bis(chloromethyl) ether of 1,2-propanediol, preparation, properties, reaction with sodium alkoxides, 738.

2) Bis(chloromethyl)ether of 1,3-propanediol, preparation, properties, reaction with sodium alkoxides, 739.

$C_5H_{11}O_2Cl$. 2-Chloroethyl methyl acetal, preparation, properties, hydrolysis, 928.

5. IV

$C_5H_6OSF_6$. 2H-Hexafluoropropyl-2-hydroxyethyl sulfide, preparation, properties, 255.

$C_5H_{12}O_2PCl$. Ethyl(chloromethyl)ethylphosphinate, preparation, properties, 766.

$C_5H_{12}O_3PCl$. Ester of chloromethylphosphonic acid, formation, 769.

Group C_6

6. I

C_6H_6. Benzene, hydrogenation and dehydrogenation with nickel catalysts, influence of carrier, 85; formation from cyclopentane and methylcyclopentane, 243; decomposition of $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ in, 272; polycondensation with 1-bromo-3-chloropropane, 307; reaction with acetylene, 479;

formation on catalytic hydrogenation of isoprene, 603; formation from 1-octene, 614; formation on catalytic hydrocondensation of cyclohexene, 635; formation from hexane, 780, heptane, 781, octane, 784.

C_6H_8. Methylcyclopentadiene, preparation, properties, 619.

C_6H_{10}. 1) Cyclohexene, reactions in contact with activated Troshkov clay, properties, formation of aromatic hydrocarbons, isomerization, cracking, 607; preparation, properties, hydrocondensation catalysis, 631.

2) 1-Methylcyclopentene, preparation, properties, oxidation, 618.

C_6H_{12}. 1) Cyclohexane, activity of compressed catalysts on the dehydrogenation of, 28; hydrogenation and dehydrogenation with nickel catalysts, influence of carrier, 85; properties, catalytic reactions under a pressure of hydrogen at high temperature, 243; formation on catalytic hydrocondensation of cyclohexene 635; formation from carbon monoxide and hydrogen, 914.

2) Methylcyclopentane, formation from cyclopentane and cyclohexane; properties, catalytic reactions under a pressure of hydrogen at high temperature, 243; formation from carbon monoxide and hydrogen, 914.

C_6H_{14}. 1) Hexane, and isomers, formation from cyclopentane, and cyclohexane, 243; preparation, properties, high-temperature contact-catalysis reactions in presence of hydrogen at high pressure, 779; formation from octane, 784.

2) 2-Methylpentane, formation from octane, 784; formation from carbon monoxide and hydrogen, 914.

3) 3-Methylpentane, formation from carbon monoxide and hydrogen, 914; preparation, properties, hydrogen exchange with heavy sulfuric acid, 924.

4) 2,3- and 2,2-Dimethylbutanes, formation from hexane, 780.

5) 2,2-Dimethylbutane, frequencies of valency vibrations, 269.

6) 2- and 3-Methylpentanes, formation from hexane, 780.

6. II

$C_6H_4O_2$. p-Benzoquinone, condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone, 1,2,3,4,4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol, 823, 824; condensation with 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinyl-naphthalene, 967.

C_6H_5O. 2-Cyclohexenone, condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinylnaphthalenone, 817.

C_6H_5Cl. Chlorobenzene, hydrolysis to phenol in presence of silica gel, 842.

C_6H_5I. Iodobenzene, reaction with mercury, 595.

C_6H_5Li. Phenyllithium, preparation, 113, 117.

C_6H_6O. Phenol, reaction with methyl-β-chlorovinylketone, 431; from chlorobenzene, in presence of silica gel, 843.

$C_6H_6O_2$. Resorcinol, reaction with acetoacetic ester, 675.

$C_6H_6O_4$. Terephthalic acid, formation from cyclopentane, 244.

C_6H_7N. Aniline, reaction with ethynyldimethylvinylmethanol, 275; product with (chloroacetamidemethylphosphonic acid, formation, 1000.

C_6H_8O. 1) 1,5-Hexadien-3-one, reaction with diethylamine, dibutylamine, to form amino ketones, 290.

2) 2-Methyl-2-cyclopenten-1-one, preparation, properties, semicarbazone, oxime, ozonization, 795; condensation with dienones, 827.

3) 2-Cyclohexen-1-one, preparation, properties, 796; condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)- and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthaleneones, 817; condensation with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, 980.

$C_6H_8N_2$. 1) 1-Methyl-2(1H)-pyridonimine, relative basicity of nitrogen atoms, absorption spectrum, 129.

2) 2-Methylaminopyridine, relative basicity of nitrogen atoms, absorption spectrum, preparation, 129.

$C_6H_8O_3$. Ethyl acetoacetate, condensation with 3-camphenilanecarboxaldehyde, 727.

$C_6H_{10}O$. 1) Mesityl oxide, condensation with 3-camphenilanecarboxaldehyde, 731.

2) Methylcyclopentanone, formation, 793.

3) 2-Methylcyclopentanone, preparation, properties, 2,4-dinitrophenylhydrazone, 619.

$C_6H_{10}O_2$. 1) Vinyl butyrate, preparation, properties, 499.

2) Acetoacetic ester, reaction with resorcinol, 675.

$C_6H_{10}O_3$. Vinyl β-hydroxybutyrate, preparation, properties, hydrolysis, 499.

$C_6H_{10}O_4$. 1) Adipic acid, condensation with ethylene glycol, 1,20-eicosanediol, 849; reaction with N,N'-hexamethylenebisacetamide, 672.

2) Diethyl oxalate, condensation with 3a-, 4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone 835.

$C_6H_{10}O_6$. Glucosone, oxidation, 342.

$C_6H_{10}O_7$. 2-Ketogluconic acid, formation from glucosone, 342.

$C_6H_{11}N$. Diallylamine, complex compounds of platinum with, preparation, reactions, structure, 209.

$C_6H_{12}O$. 1) Butyl vinyl ether, reaction with ethanethiol, 2-butoxyethylethanethiolthioacetic acid, 328; use in vinylation of monocarboxylic and hydroxy acids, 499; reaction with triethylsilanol, 838; preparation, properties, copolymerization with methacrylic acid, 934; reactions with acetylenic alcohols to form acetals, 947.
2) Isobutyl vinyl ether, properties, reaction with 2-chloroethanol, 927; reaction with acetylenic alcohols to form acetals, 947; reaction with triethylsilanol, 838.
3) Cyclohexanol, dehydration to cyclohexene, 631.
$C_6H_{12}O_2$. Trans-1-methyl-1,2-cyclopentanediol, preparation, dehydration, 619.
$C_6H_{12}O_3$. Paraldehyde, condensation with N-p-tolyl-2-naphthylamine to form quaternary salts, 949.
$C_6H_{12}N_4$. Hexamethylenetetramine, reaction with benzoylbromoacetaldehyde, 889.
$C_6H_{14}O$. 1-Methylcyclohexanol, preparation, properties, dehydration, 620.
$C_6H_{14}O_2$. Hexamethylene glycol, polycondensation with sebacic acid, 483.
$C_6H_{14}O_3$. 1) Acetaldehyde ethyl 2-hydroxyethyl acetal, reaction with ethylene glycol, 91; action of heat, 92.
2) Mono(isopropoxymethyl) ether of ethylene glycol, preparation, properties, 739.
$C_6H_{14}O_4$. Bis(methoxymethyl) ether of ethylene glycol, preparation, properties, 739.
$C_6H_{16}N_2$. 1,6-Hexanediamine, reaction with dibutyl adipate, 671.
$C_6H_{16}Si$. Diethyldimethylsilane, preparation, properties, Raman spectra, 267.

6. III

C_6H_4LiBr. p-Bromophenyllithium, preparation, properties, 118.
C_6H_4LiCl. p-Chlorophenyllithium, preparation, properties, 119.
C_6H_5HgI. Phenylmercury iodide, preparation, 595.
C_6H_8NCl. Aniline hydrochloride, reaction with antimony trichloride, 271.
$C_6H_8OF_6$. 1) 2H-Hexafluoropropyl propyl ether, preparation, properties, 255.
2) 2H-Hexafluoropropyl isopropyl ether preparation, properties, 255.
$C_6H_9N_2I$. Methiodide of aminopyridine, relative basicity of nitrogen atoms, absorption spectrum, 129.
$C_6H_9O_3Br$. Ethyl 2-bromoacetoacetate, reaction with mercury, 592.
$C_6H_{11}ON$. 1) Caprolactam, formation on hydrolysis of vinylcaprolactam, 97.
2) 4-Dimethylamino-3-buten-2-one, preparation, properties, picrate, reaction with acetic acid, 884.
$C_6H_{11}O_2Br$. Ethyl 2-bromobutyrate, reaction with mercury, 592.
$C_6H_{12}O_2Cl_2$. Acetaldehyde bis(2-chloroethyl) acetal, reaction with dimethylaniline, preparation action, of alcoholic KOH, 644; hydrolysis with sodium carbonate solution, 93.
$C_6H_{13}N_4Br$. Reaction product of benzoylbromoacetaldehyde and hexamethylenetetramine, formation, properties, structure, 889.
$C_6H_{14}OS$. 1) 1-Ethoxy-1-(ethylthio)ethane, preparation, properties, reaction with alcoholic mercuric chloride, 327.
2) 1-Ethoxy-2-(ethylthio)ethane, preparation, properties, 328.
3) 1-Butoxyethylethanethiol, reaction with butyl vinyl ether, 333.
$C_6H_{14}O_2S$. Sulfoxide from oxidation of 1-ethoxy-2-(ethylthio)ethane, preparation, properties, 329.
$C_6H_{15}ON$. 2-(Diethylamino)ethanol, preparation, properties, vinylation, 336.
$C_6H_{15}O_3P$. Triethyl phosphite, preparation, properties, complex with CuI, reaction with propionyl chloride, 434.
$C_6H_{16}SiO$. Triethylsilanol, reaction with butyl vinyl ether, isobutyl vinyl ether, 838.

6. IV

$C_6H_{15}O_2SP$. Diethyl ethylphosphonothionate, preparation, properties, hydrolysis, 154.
$C_6H_{15}O_2PS_2$. O,O-Dipropyl and diisopropyl-hydrogen phosphorothiolothionate, preparation, properties, lead salts, titration, oxidation with iodine, 110.
$C_6H_{15}O_3SiCl$. Triethoxy monochlorosilane, preparation, properties, 436.

Group C_7
7. I

C_7H_8. Toluene, formation from cyclopentane methylcylcopentane and cyclohexane, 243; content in dehydrogenation product of isomerizate from ethylcyclopentane, 252; formation from 1-octene, 614; formation on catalytic hydrocondensation of cyclohexene, 635; formation from hexane, heptane, octane, 781.
C_7H_{10}. Ethynyldimethylvinylmethanol, reaction with aniline, 275.
C_7H_{12}. 1) 1-Methylcyclohexene, preparation, properties, oxidation, 620.
2) 4-Methylcyclohexene, reactions in contact with activated Troshkov clay, formation of aromatic hydrocarbons, isomerization, cracking, properties, 607.
C_7H_{14}. 1) Ethylcyclopentane, isomerization to methylcyclohexane, 251.
2) Methylcyclohexane, formation from carbon

monoxide and hydrogen. 914; formation from ethylcyclopentane, 251.

C_7H_{16}. 1) Heptane, activity of compressed catalysts on dehydrocyclization of, 27; preparation, properties, high-temperature contact-catalysis reactions in presence of hydrogen at high pressure, 779; formation from octane, 784; chromatography with silica gel, 843.

Heptane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 923.

2) 2,2- and 2,3-Dimethylpentane, formation from carbon monoxide and hydrogen, 914.

3) 2- and 3-Methylhexanes, formation from carbon monoxide and hydrogen, 914.

4) 3-Methylhexane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 925.

5) 2,2,3-Trimethylbutane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 924.

7. II

C_7H_6O. Benzaldehyde, formation from styrene, 322; reaction with dialkyl hydrogen phosphites and ammonia, 769.

$C_7H_6O_2$. Benzoic acid, formation from cyclopentane, 244; formation from Hofmann reaction with amide of N-benzoyl-β-piperonyl-β-alanine, 463; formation on reaction of bromoform with mercury in presence of benzoyl peroxide, 595.

C_7H_7Br. Benzyl bromide, reaction with mercury, 592.

C_7H_7Cl. Benzyl chloride, reaction with butyllithium, 263.

C_7H_7Li. 1) Benzyllithium, preparation, properties, 263.

2) o, m, and p-Tolyllithium, preparation, properties, 116.

$C_7H_7O_2$. 3,5-Dimethyl-3-cyclopentene-1,2-dione, condensation with dienones, 827.

$C_7H_8O_2$. 2,4-Dimethyl-Δ^2-cyclopentene-1,5-dione, preparation, 469.

C_7H_9O. 2,4-Dimethyl-2-cyclopenten-1-one, preparation, properties, 796; condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone, 799; condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)- and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenones, 817; condensation with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, 980.

$C_7H_{10}O$. 1) Dimethylcyclopentenone, deutero compound, preparation, properties, structure, ozonization, oxidation, 467.

2) 2-Methyl-2-cyclohexen-1-one, preparation, properties, ozonization, 792; condensation with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)- and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenones, 817; properties, condensation with 1,3-butadiene, 961.

3) 2-Methyl-1,5-hexadien-3-one, cyclization with the aid of deuterium, 103; reaction with diethylamine dibutylamine, to amino ketones, 290.

$C_7H_{10}N_2$. 1-(2-Hydroxyethyl)-2(1H)-pyridonimine, relative basicity of nitrogen atoms, absorption spectrum, 129.

$C_7H_{11}Cl_3$. 1,1,7-Trichloroheptene, formation, properties, 880.

$C_7H_{12}O$. 1) 2-Methylcyclohexanone, preparation, properties, conversion to 2-methyl-2-cyclohexen-1-one, bromination, 792.

2) 2-Methylcyclohexanone-1, preparation, properties, 2,4-dinitrophenylhydrazone, 620.

$C_7H_{12}Cl_2$. 1,1-Dichloroheptene, preparation, properties, 880.

$C_7H_{12}Cl_4$ Tetrachloroheptane, splitting off HCl, 880.

$C_7H_{12}O_2$ 1) Methoxy ketone, conversion to diamino ketone, 290.

2) Vinyl valerianate, preparation, properties, 499.

$C_7H_{13}Cl$. 3-Chloro-2,4-dimethyl-1-pentene, preparation, properties, Grignard reagent, reaction with 2,4-dimethyl-3-pentanone, ethylformate and amyl butyrate, 910.

$C_7H_{13}Cl_3$. Trichloroheptane, removal of HCl from, 880.

$C_7H_{14}O$. 1) 2,4-Dimethyl-3-pentanone, reaction with Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene, 910.

2) 4-Heptanone, properties, reductive amination, 81.

3) 2-Methylcyclohexanol, preparation, properties, conversion to ketone, oxidation, 792.

$C_7H_{14}O$. Isoamyl vinyl ether, properties, reaction with 2-chloroethanol, 927.

$C_7H_{14}O_2$. Amyl acetate, decomposition of C_6 ($C_6H_5N_2Cl_2\cdot SbCl_3$ in, 272.

$C_7H_{14}Si$. Diallylmethylsilane, properties, Raman spectrum, 159.

$C_7H_{16}O_3$. 1) Mono(isobutoxymethyl) ether of ethylene glycol, preparation, properties, alcoholysis, 740.

2) 1,3,3-Trimethoxybutane, preparation, 74.

$C_7H_{16}O_4$. Bis(methoxymethyl)ether of 1,2-propanediol, preparation, properties, 740; of 1,3-propanediol, preparation, properties, 741.

$C_7H_{17}N$. 1-Propylbutylamine, reductive amination product of 4-heptanone, formation, properties, 83.

$C_7H_{18}Si$. Triethylmethylsilane, preparation, properties, Raman spectra, 267.

7. III

C_7H_5OCl. Benzoyl chloride, reaction with triethyl phosphite, 769.

$C_7H_{10}OF_6$. Butyl 2H-hexafluoropropyl ether, preparation, properties, 255.

$C_7H_{11}O_4Br$. Diethyl bromomalonate, reaction with mercury, 592.

$C_7H_{13}MgCl$. Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene, reaction with 2,4-dimethyl-3-pentanone, ethyl formate and amyl butyrate, 910.

$C_7H_{15}NS$. 2,5-Dimethyltetrahydro-1-thiopyran-4-amine, preparation, properties, hydrochloride, acetyl derivative, benzoyl derivative, oxidation of hydrochloride and benzoyl derivative, 457.

$C_7H_{15}OCl$. 2-Chloroethylpropyl and isopropylacetal, preparation, properties, hydrolysis, 928.

$C_7H_{15}O_4P$. Product of reaction of triethyl phosphite and propionyl chloride, ethyl ester of propionylphosphinic acid, formation, properties, analysis, reaction sodium nitroprusside, semicarbazone, diethylacetal, 435.

$C_7H_{16}ON_2$. Hydrazide of heptanoic acid, preparation, reaction with carbonylchloride, 63.

7. IV

$C_7H_7OPCl_2$. (Chloromethyl)phenylphosphinic chloride, preparation, properties, conversion to acid, reaction with alcohol, 766.

$C_7H_8O_2PCl$. (Chloromethyl)phenylphosphinic acid, preparation, properties, 766.

$C_7H_{10}PNO_3$. α-Aminobenzylphosphonic acid, preparation, properties, 774.

$C_7H_{11}NPtCl_2$. Dichloro(diallylamine)platinum, preparation, reaction with ammonia, pyridine, thiourea, HCl, caustic alkalies, 209.

$C_7H_{11}F_4ON$. Diethylamide of 2H-tetrafluoropropionic acid, preparation, properties, 260.

$C_7H_{13}ONS$. 1) 2,5-Dimethyltetrahydro-1-thiopyran-4-one oxime, preparation, conversion, to amine, 457.
2) Lactam from rearrangement of 2,5-dimethyltetrahydro-1-thiopyran-4-one, oxime, preparation, 458.

$C_7H_{13}O_3NS$. 1) Oxidation product of lactam from 2,5-dimethyltetrahydro-1-thiopyran oxime, 458.
2) Oxime of dihydroxy-2,5-dimethyltetrahydrothiopyran-4-one, preparation, 457.

$C_7H_{15}NSCl$. Hydrochloride of 2,5-dimethyltetrahydro-1-thiopyran-4-amine. Preparation, properties, oxidation, 457.

$C_7H_{15}O_2NS$. Thioaminoacid, preparation, 459.

7. V

$C_7H_{16}ONSCl$. Aminosulfoxide hydrochloride of 2,5-dimethyltetrahydro-1-thiopyran, preparation, 458.

$C_7H_{16}O_2NSCl$. Aminosulfone hydrochloride of 2,5-dimethyltetrahydro-1-thiopyran, preparation, 458.

Group C_8

8. I

C_8H_6. Phenylacetylene, reactionwith ethyllithium, 358.

C_8H_8. Styrene, formation by catalytic dehydrogenation of ethylbenzene and ethylcyclohexane, 895, 903; properties, catalytic polymerization in presence of ferric chloride and stannic chloride, 319; theoretical and experimental yields in the catalytic dehydrogenation of ethylbenzene, 365.

C_8H_{10}. 1) Xylene, formation from cyclopentane, methylcyclopentane and cyclohexane, 243; formation from hexane, heptane, octane, 781.
2) Ethylbenzene, catalytic dehydrogenation to styrene, 365; properties, catalytic dehydrogenation of, 895, 903.

C_8H_{16}. 1) 1-Octene, reactions in contact with activated Troshkov clay, formation of aromatic hydrocarbons, isomerization, cracking, properties, 607.
2) Ethylcyclohexane, properties, catalytic dehydrogenation to ethylbenzene and styrene, 895; catalytic dehydrogenation to ethylbenzene, 903.

C_8H_{18}. 1) 2,2-Dimethylhexane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 924.
2) 2,3-Dimethylhexane, formation from octane, 784.
3) 3-Ethyl-3-methylpentane, frequencies of valency vibrations, 269.
4) 4-Methylheptane, formation from octane, 784.
5) Octane, preparation, properties, high-temperature contact-catalysis reactions in presence of hydrogen at high pressure, 779.
6) 2,2,4-Trimethylpentane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 925.

8. II

$C_8H_4O_3$. Phthalic anhydride, reaction with aminomethylphosphonic acid, 1000.

C_8H_5Li. Phenylethynyllithium, preparation, properties, 358.

$C_8H_6O_3$. Piperonal reaction with dialkyl hydrogen phosphites and ammonia, 769.

$C_8H_6O_4$. Terephthalic acid, formation, 309.

C_8H_8O. 1) Acetophenone, condensation with 3-camphenilanecarboxaldehyde, 731.
2) p-Anisaldehyde, reaction with dialkyl hydrogen phosphites and ammonia, 769.
3) p-Tolualdehyde, reaction with dialkyl hydrogen phosphites and ammonia, 769.

$C_8H_8O_2$. Phenylacetic acid, formation from benzyl chloride and butyllithium, 263.

$C_8H_8O_3$. 1) Acetyl resorcinol, preparation. reaction with NaOH, 495.
 2) 2',6'-Dihydroxyacetophenone, preparation, methylation, 675.
 3) Vanillin, reaction with dialkyl hydrogen phosphites and ammonia, 769.

C_8H_9Br. (2-Bromoethyl)benzene, reaction with mercury, 592.

$C_8H_{11}N$. Dimethylaniline, reaction with acetaldehyde bis(2-chloroethyl)acetal, 644.

$C_8H_{14}O_2$. 1) 5-Methoxy-2-methyl-1-hexen-3-one, reaction with diethylamine dibutylamine to form amine ketones, 290.
 2) Vinyl caproate, preparation, properties, hydrogenation, hydrolysis, 499.

$C_8H_{14}O_4$. Bis(methoxymethyl)ether of 2-butyne-1,4-diol, preparation, properties, 743.

$C_8H_{14}O_4$. Diethyl succinate, 2,3-d_2, preparation, polyester exchange reaction with polyhexamethylene sebacate, 125.

$C_8H_{16}O$. 1) Hexyl vinyl ether, copolymerization with ethyl vinyl ether, 647; properties, ionic polymerization of, 941.
 2) Copolymerization product of hexyl vinyl ether and ethyl vinyl ether, formation, properties, 649.
 3) 2-Octanone, properties, reductive amination, 81.

$C_8H_{16}O_3$. Methoxy ketone, conversion to diamino ketone, 290.

$C_8H_{17}Si$. Triethyl(2-methylpropenyl)silane, properties, Raman spectrum, 159.

$C_8H_{18}O_3$. 1) Mono(butoxymethyl) ether of 1,2-propanediol, preparation, properties, 741.
 2) Bis(2-ethoxyethyl)ether, preparation, synthesis of lithium aluminum chloride in, 527.
 3) Acetaldehyde 2-ethoxy ethyl acetal, preparation, properties, 644.

$C_8H_{18}O_4$. Bis(methoxymethyl)ether of 1,3-butanediol, preparation, properties, 742.

$C_8H_{19}N$. Dibutylamine, reaction with 2-methyl-1,5-hexadien-3-one, also, 5-methoxy-2-methyl-1-hexen-3-one, to form amino ketone, 290; 5-methyl-1,4-hexadien-3-one, 1-methoxy-5-methyl-4-hexen-3-one, 1-methoxy-5-methyl-3-hexanone, 291.

8. III

C_8H_7OBr. 1) Bromomethyl phenyl ketone, reaction with mercury, 593.
 2) Bromo(phenyl)acetaldehyde, reaction with mercury, 593.

C_8H_7HgBr. (Bromomercuri)phenylacetic acid, (l)-menthyl esters of, preparation, properties, 583.

$C_8H_7O_2Br$. Bromo(phenyl)acetic acid, reaction with menthol, 585.

$C_8H_{13}ON$. Vinylcaprolactam, reaction with water in presence of hydrogen peroxide hydrolysis, polymerization, 97.

$C_8H_{13}N_2I$. Methiodide of 2-dimethylaminopyridine, relative basicity of nitrogen atoms, absorption spectrum, 129.

$C_8H_{14}N_2O_2$. 5-Hexyl-1,3,4-oxadiazol-2(3H)-one, preparation. Action of ammonia, hydrolysis, 61.

$C_8H_{15}ON$. 4-Diethylamino-3-buten-2-one, preparation, properties, picrate, 885.

$C_8H_{15}ON_3$. 5-Hexyl-1 H-1,2,4-triazol-3(2H)-one. preparation, 65.

$C_8H_{15}N_3S_2$. Thiosemicarbazone of 2,5-dimethyltetrahydro-1-thiopyran-4-one, preparation, 459.

$C_8H_{16}O_2S$. 2-Butoxyethyl thiolacetate, preparation, properties, 333.

$C_8H_{17}OCl$. 2-Chloroethyl isobutyl acetal, preparation, properties, hydrolysis, 928.

$C_8H_{17}ON$. 1) 1-Dimethylamino-1-hexen-3-one, preparation, properties, 885.
 2) Vinyl ether of 2-(diethylamino)ethanol, preparation, properties, hydrogenation, formation of acetals, 337.

$C_8H_{17}O_2N_3$. 1-Heptanoylsemicarbazide, preparation, action of KOH, 65.

$C_8H_{18}OS$. 1) 1-Butoxy-1-(ethylthio)ethane, preparation, properties, 328, 331.
 2) 1-Butoxy-2-(ethylthio)ethane, preparation, properties, oxidation, 329.

$C_8H_{18}O_2S$. 1-Ethoxyethyl-2-ethoxyethyl sulfide, preparation, properties, 331.

$C_8H_{19}ON$. Ethyl ether of 2-(diethylamino)ethanol, preparation, properties, 337.

$C_8H_{19}OP$. Dibutyl hydrogen phosphite, reaction with piperonal, benzaldehyde, 769.

8. IV

$C_8H_{10}O_2PCl$. Methyl(chloromethyl)phenylphosphinic acid, preparation, properties, 766.

$C_8H_{12}NPO_3$. α-Amino-p-methylbenzylphosphonic acid, preparation, 774.

$C_8H_{12}NPO_4$. α-Amino-p-methoxybenzylphosphonic acid, preparation, 775.

$C_8H_{12}NPO_5$. α-Amino-4-hydroxy-3-methoxybenzylphosphonic acid, preparation, 776.

$C_8H_{15}O_2N_3S_2$. Thiosemicarbazone of dihydroxy-2,5-dimethyltetrahydro-1-thiopyran-4-one, preparation, 459.

$C_8H_{15}O_3N_3S$. Semicarbazone of dihydroxy-2,5-dimethyltetrahydro-1-thiopyran-4-one, preparation, 459.

$C_8H_{16}NPO_5$. α-Amino-3,4-methylenedioxybenzylphosphonic acid, preparation, 776.

$C_8H_{17}O_4PS$. Diethyl ethoxycarbonylmethylphosphonothionate, preparation, properties, hydrolysis, 155.

$C_8H_{20}O_4P_2S_4$. Disulfide obtained from O,O-diethyl hydrogen phosphorothiolothionate, 111.

8. V

$C_8H_{20}O_4P_2S_4Pb$. 1) Lead bis(O,O-diethylphosphorothiolothionate), preparation, 110.
2) Lead salt of reaction product of sodium O,O-diethyl phosphorothiite and sulfur, 154.
$C_8H_{25}N_2P_2O_6I$. Product of reaction of aminomethylphosphonic acid and methyl iodide, 1000.

Group C_9

9. II

C_9H_9Br. Cinnamyl bromide, reaction with mercury, 593.
C_9H_9Cl. Cinnamyl chloride, reaction with mercury, 592.
$C_9H_{11}Br$. (3-Bromopropyl)benzene, preparation, reaction with benzene, 307.
$C_9H_{16}O_2$. Ethyl 1,1-dimethyl-2-propynyl acetal, preparation, properties, hydrolysis, 945.
$C_9H_{16}Cl_4$ Tetrachlorononane, removal of HCl from, 880.
$C_9H_{17}Cl_3$. 1,1,9-Trichlorononene, preparation, properties, 880.
$C_9H_{18}O_2$. Amyl butyrate, reaction with Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene, 911.
$C_9H_{16}O_4$. Butoxyethylidene lactate, preparation, properties, 502.
$C_9H_{20}O_2$. 1) Dibutoxymethane, preparation, properties, 739.
2) Diisobutoxymethane, preparation, properties, 740.
$C_9H_{20}O_3$. Ethyl ester of orthopropionic acid, reaction with phosphorous trichloride, 433.
$C_9H_{20}O_4$. 1) Bis(ethoxymethyl)ether of 1,2-propanediol, preparation, properties, 741.
2) Bis(ethoxymethyl)ether of 1,3-propanediol, preparation, properties, alcoholysis, 742.

9. III

$C_9H_6O_4N_2$. 5-Piperonyl-1,3,4-oxadiazol-2(3H)-one, preparation, 463.
$C_9H_6F_6O$. 2H-Hexafluoropropyl phenyl ether, preparation, properties, 255.
$C_9H_7O_2Br$. Benzoylbromoacetaldehyde, reaction with hexamethylenetetramine, urea, 889.
C_9H_9HgBr. Cinnamylmercury bromide, preparation, properties, 593.
$C_9H_{15}ON$. 1) 2-Methyl-4-ketoperhydro-1-pyrindine, preparation, properties, picrate, isomerization, 450.
2) 4-Piperidino-3-buten-2-one, preparation, properties, picrate, 885.
$C_9H_{17}ON$. 1-Dimethylamino-5-methyl-1-hexen-3-one, preparation, properties, 885.
$C_9H_{19}OCl$. 2-Chloroethyl isopentyl acetal, preparation, properties, hydrolysis, 928.

9. IV

$C_9H_8NPO_5$. Phthalimidomethylphosphonic acid, preparation, 1000.
$C_9H_{12}O_2PCl$. Ethyl(chloromethyl)phenylphosphinate, preparation, properties, 766.
$C_9H_{14}N_2O_4Cl$. Addition product of (chloroacetamido)-methylphosphonic acid and aniline, formation 1000.
$C_9H_{17}ONS$. Acetyl derivative of 2,5-dimethyltetrahydro-1-thiopyran-4-amine, preparation, 458.

Group C_{10}

10. I

$C_{10}H_{12}$. Tetrahydronaphthalene, formation, 307.
$C_{10}H_{16}$. 1) Allo-ocimene, preparation, properties, autoxidation, 423.
2) Camphene, formation from α-pinene, 750.
3) Δ^3-Carene, isomerization by the action of silica gel under conditions of adsorptional analysis, 751.
4) α-Pinene, isomerization by the action of silica gel under conditions of adsorptional analysis, 749.
5) Terpinolene, formation from dipentene α-pinene, Δ^3-carene, 750.
6) Dipentene, formation from α-pinene, 749; isomerization by the action of silica gel under conditions of adsorptional analysis, 750.
$C_{10}H_{18}$. 1-Butyl-2-methylcyclopentene, preparation, properties, hydrogenation, 622.
$C_{10}H_{20}$. 1-Butyl-2-methylcyclopentane, preparation, separation into cis and trans isomers, 622.

10. II.

$C_{10}H_7I$. 1-Iodonaphthalene, reaction with mercury, 595.
$C_{10}H_7Li$. 1-Naphthyllithium, preparation, properties, 119.
$C_{10}H_8O$. β-Naphthol, reaction with methyl-β-chlorovinylketone, 430.
$C_{10}H_8O_3$. 7-Hydroxy-4-methylcoumarin, preparation, acetylation, action of NaOH, 495.
$C_{10}H_{12}O$. p-Isopropylbenzaldehyde, reaction with dialkyl hydrogen phosphites and ammonia, 769.
$C_{10}H_{12}O_2$. 2,6-Dimethoxystyrene polymer, preparation, 497.
$C_{10}H_{12}O_3$. 1) 2,6-Dimethoxyacetophenone, preparation, polymerization, reduction, 496.
2) 2',6'-Dimethoxyacetophenone, preparation, action of methylmagnesium iodide, 675.
$C_{10}H_{14}O_2$. Dienone from reaction of methoxy ketone

with p-toluenesulfonic acid, preparation, properties, 289.

$C_{10}H_{14}N_2$. Anabasine, isolation from *Anabasis aphylla*, oxidation, fission, ammination, sulfonation, cyanethylation, reaction with aliphatic oxides, 471.

$C_{10}H_{16}O$. 1) 3-Camphenilanecarboxaldehyde, condensation with ketones, ethyl acetate and ethyl acetoacetate, 727.
2) β-Decalone, condensation with ethyl chloroacetate, 231.

$C_{10}H_{16}O_2$. 1) Secondary oxide of allo-ocimene, preparation, determination of degree of unsaturation, active hydrogen, peroxide oxygen, color reaction with pyridine, reaction with manganese chloride, methanol, hydrogenation, hydration, 425.
2) Polyperoxide of allo-ocimene, preparation, nature of oxygen bonds, determination of degree of unsaturation, behavior on storage, and heating, 423.

$C_{10}H_{18}O$. Unsaturated ketone, formation, semicarbazone, 910.

$C_{10}H_{18}O_2$. Isopropyl 1,1-dimethyl-2-propynyl acetal, preparation, properties, alcoholysis, hydrolysis, 946.

$C_{10}H_{18}O_4$. 1) Diethyl adipate, reaction with N,N'-hexamethylenebisacetamide, ethylene glycol, 672; preparation, properties, reaction with sodium and alcohol, 794.
2) Sebacic acid, polycondensation with hexamethylene glycol, 483.

$C_{10}H_{18}O_6$. Bis(2-hydroxyethyl)adipate, preparation, determination of hydroxyl groups, preparation of polyester, 670.

$C_{10}H_{20}O_2$. N,N'-hexamethylenebisacetamide, action of adipic acid, diethyl adipate, 672.

$C_{10}H_{20}O_4$. Unsaturated aliphatic tetrahydric terpene alcohol, formation, acetylation, 427.

$C_{10}H_{22}O$. 1) Diisopentyl ether, decomposition of $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ in, 272.
2) 1-Butyl-2-methylcyclopentanol, preparation, properties, dehydration, 621.

$C_{10}H_{22}O_2$. 1) Saturated aliphatic terpene glycol, formation, 427.
2) Dibutylacetal, formation, properties, 502.

$C_{10}H_{22}O_3$. Acetaldehyde butyl 2-ethoxyethyl acetal, preparation, properties, 645.

$C_{10}H_{22}O_4$. 1) Bis(2-ethoxyethyl)acetal, of acetaldehyde, preparation, properties, 645.
2) Bis(ethoxymethyl) ether of 1,3-butanediol, preparation, properties, 742.

10. III

$C_{10}H_7HgI$. 1-Naphthylmercury iodide, preparation, 595.

$C_{10}H_8O_2N_2$. 1) 2-Amino-5-benzoyloxazole, preparation, properties, hydrochloride acetyl derivative, chemical reactions, 890.
2) 4-Phenyl-2,5-pyrimidinediol, preparation, diacetyl derivative, monobenzyl ether, 891.

$C_{10}H_{10}O_3N_2$. 5-Piperonylglyoxalidone, preparation, 463.

$C_{10}H_{11}O_2Br$. Ethyl bromo(phenyl)acetate, reaction with mercury, 593.

$C_{10}H_{14}ON_2$. 2-Amino-5-benzoyloxazolidine, (3-phenylpropylurea), formation, hydrogenation, 890.

$C_{10}H_{17}ON$. 1,2-Dimethyl-4-ketoperhydro-1-pyrindine, preparation, properties, picrate, isomerization, 450.

$C_{10}H_{17}O_2Cl$. Dichlorohydrin formed from allo-ocimene secondary oxide and manganese chloride, 426.

$C_{10}H_{18}O_2Cl_2$. Dichlorohydrin formed from allo-ocimene secondary oxide and manganese chloride, 426.

$C_{10}H_{19}NO$. Lupinine, isolation from *Anabasis aphylla*, 471.

$C_{10}H_{22}SiO_2$. Triethylsilyl butyrate, preparation, properties, 121.

10. IV

$C_{10}H_9OFeCl_4$. 1) 1-Methylbenzopyranyl ferrichloride preparation 431.
2) 2-Methylbenzopyranyl ferrichloride, preparation, 432.

$C_{10}H_9O_2N_2Cl$. Hydrochloride of 2-amino-5-benzoyloxazole, formation, 890.

$C_{10}H_9O_3N_2Na$. Sodium salt of the enolate of phenyl-3-ureido-1,2-propanedione, preparation, 891.

$C_{10}H_{11}O_2HgBr$. Ethyl(bromomercuri)phenylacetate, preparation, properties, symmetrization, reaction with acetyl chloride, 593.

$C_{10}H_{14}NPO_5$. Ethyl hydrogen α-amino-3,4-methylenedioxybenzylphosphonate, preparation hydrochloride, 775.

$C_{10}H_{16}NPO_3$. α-Amino-p-isopropylbenzylphosphonic acid, preparation, 775.

Group C_{11}

11. II

$C_{11}H_8O_3$. 4-Methylumbelliferone, preparation, acetylation, 675.

$C_{11}H_9O_2$. Hexahydro-8a-methyl-1,6-(2H,5H)-naphthalenedione, preparation, 78.

$C_{11}H_{13}N_2$. 1-Benzyl-2(1H)-pyridonimine, relative basicity of nitrogen atoms, absorption spectrum, 129.

$C_{11}H_{13}N_3$. 1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)pyridonimine, preparation, relative basicity of nitrogen atoms, absorption spectrum, 129.

$C_{11}H_{14}O$. 1,2,3,4-Tetrahydro-6-methoxynaphthalene, preparation, oxidation, 981.

$C_{11}H_{14}O_2$. 2,6-Dimethoxy-α-methylstyrene, preparation, 678.

$C_{11}H_{16}O$. Cis-3,4,4a,5,8,8a-Hexahydro-8a-methyl-1(2H)-naphthalenone, preparation, properties, semicarbazone, hydrogenation, condensation with acetylene, 961.

$C_{11}H_{18}O$. 1) Cis-octahydro-8a-methyl-1(2H)-naphthalenone, preparation, properties, dinitrophenylhydrazone, 961.

2) Decahyro-2-naphthaldehyde, preparation, condensation with malonic acid, 231; semicarbazone, 232.

$C_{11}H_{18}O_3$. 1) Methoxy ketone from isomerization of tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol, preparation, properties, hydrogenation, oxidation, reaction with p-toluenesulfonic acid, dimethylamine, piperidine, 289.

2) Tetrahydro-2-methyl-4(vinylethynyl)pyran-4-ol, preparation, properties, isomerization, 289.

$C_{11}H_{20}O_2$. 1) Butyl 1,1-dimethyl-2-propynyl acetal, preparation, properties, 947.

2) Isobutyl 1,1-dimethyl-2-propynyl acetal, preparation, properties, hydrolysis, 947.

$C_{11}H_{22}O_3$. Hydrogenation product of methoxy ketone, preparation, properties, 289.

$C_{11}H_{24}O_4$. 1) Bis(isopropoxymethyl)ether of 1,2-propanediol, preparation, properties, 741.

2) Bis(isopropoxymethyl) ether of 1,3-propanediol, preparation, properties, 742.

$C_{11}H_{25}O_5P$. Diethylacetal of the ethyl ester of propionyl phosphinic acid, preparation, properties, saponification, 434.

11. III

$C_{11}H_{13}O_2Br$. Ethyl 2-bromo-2-phenylpropionate, reaction with mercury, 592.

$C_{11}H_{15}O_4P$. Diethylbenzoylphosphonate, form tion, p-nitrophenylhydrazone, 769.

$C_{11}H_{17}PO_4$. Diethyl α-hydroxybenzylphosphonate preparation, reaction with ammonia in presence of sodium ethoxide, 776.

$C_{11}H_{19}ON$. 1) 2,9-Dimethyl-4-ketodecahydroquinoline, preparation, properties, picrate, isomerization, 450.

2) 2,6,7a-Trimethyl-4-ketoperhydro-1-pyrindine preparation, properties, picrate, 451.

$C_{11}H_{21}ON$. Decahydro-1,2-dimethyl-4-quinolinol, preparation, 663.

$C_{11}H_{21}N_3O$. Semicarbazone of unsaturated ketone, 911.

$C_{11}H_{24}SiO_2$. Triethylsilyl isovalerate, preparation, properties, 122.

11. IV

$C_{11}H_{17}O_2PS$. Diethyl benzylphosphonothionate, preparation, properties, 155.

11. V

$C_{11}H_{19}NPO_3Cl$. 1) Reaction product of diethyl α-hydroxybenzylphosphonate and ammonia, 776.

2) Hydrochloride of diethyl α-aminobenzylphosphonate, preparation properties, 773.

Group C_{12}

12. I

$C_{12}H_{26}$. Dodecane, preparation, properties, hydrogen exchange with heavy sulfuric acid, 923.

12. II

$C_{12}H_9Li$. 4-Biphenyllithium, preparation, properties, 119.

$C_{12}H_{10}O_3$. 7-Acetoxy-4-methylcoumarin, preparation, reaction with aluminum chloride, 495.

$C_{12}H_{12}N_2$. 2-Benzylaminopyridine, preparation, relative basicity of nitrogen atoms, absorption, spectrum 129.

$C_{12}H_{12}O_3$. Triacetylbenzene, formation, 886.

$C_{12}H_{18}O_2$. Diacetylenic acetal, preparation, properties, 946.

$C_{12}H_{22}O_4$. Bis(isopropoxymethyl)ether of 2-butyne-1,4-diol, preparation, properties, 743.

$C_{12}H_{24}O$. Decyl vinyl ether, properties, ionic polymerization of, 942.

$C_{12}H_{24}O_3$. Butoxyethylidene caproate, formation, properties, 501.

$C_{12}H_{24}O_4$. Reaction product of secondary oxide of allo-ocimene and methanol, 426.

$C_{12}H_{26}O_4$. 1) Bis(butoxymethyl)ether of ethylene glycol, preparation, properties, 740.

2) Bis(isobutoxymethyl) ether of ethylene glycol, preparation, properties, 740.

3) Bis(isopropoxymethyl) ether of 1,3-butanediol, preparation, properties, 743.

12. III

$C_{12}H_{10}O_3N_2$. Acetyl derivative of 2-amino-5-benzoyloxazole, formation, transformations, 890.

$C_{12}H_{12}ON_3$. Semicarbazone of cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone, formation, properties, 961.

$C_{12}H_{12}O_4N_2$. 3-(3-Acetylureido)-1-phenyl-1,2-propanedione, preparation, properties, hydrogenation potassium salt, conversion to hydantoin, 890, 892.

$C_{12}H_{13}O_5N$. N-acetyl-β-piperonyl-β-alanine, preparation, reaction with thionyl chloride, 462.

$C_{12}H_{14}O_4N_2$. Amide of N-acetyl-β-piperonyl-β-alanine, preparation, Hofmann reaction, 462.

$C_{12}H_{14}O_5N_2$. Amide of N-carbomethoxy-β-piperonyl-β-alanine, preparation, Hofmann reaction, 463.

$C_{12}H_{15}O_8N_4$. Picrate of 4-dimethylamino-3-buten-2-one, formation, 885.

$C_{12}H_{21}ON$. 1) 1,2,6,7a-Tetramethyl-4-ketoperhydro-1-pyrindine, preparation, properties, picrate isomerization, 451.

2) 1,2,9-Trimethyl-4-ketodecahydroquinoline, preparation, properties, picrate, isomerization, 449.

$C_{12}H_{21}ON_3$. Semicarbazone of decahydro-2-naphthaldehyde, formation, 232.

$C_{12}H_{21}O_2N$. Amino ketone, preparation, properties, 289.

$C_{12}H_{21}O_3N_3$. 5-(2-Acetamidooctyl)-1,3,4-oxadiazol-2(3H)-one, preparation, action of NH_3, 63.

$C_{12}H_{24}N_4O_3$. 1) Semicarbazide derivative formed from 3-acetamidononanoic acid hydrazide, 61.

2) 1-(3-Acetamidononanoyl)-semicarbazide, preparation, 65.

$C_{12}H_{25}O_3N_3$. Hydrazide of 3-(ethoxycarbonylamino)-nonanoic acid, preparation, 64.

$C_{12}H_{26}O_2S$. 1) bis(2-Butoxyethyl)sulfide, preparation, properties, 332.

2) 1-Butoxyethyl, 2-butoxyethyl sulfide, preparation, properties, 332.

$C_{12}H_{26}Si_2O_4$. Bis(trimethylsilyl) adipate, preparation, properties, 123.

$C_{12}H_{27}O_2N$. Acetaldehyde butyl-2-(diethylamino) ethyl acetal, preparation, properties, hydrolysis, 337.

$C_{12}H_{28}SiO_2$. 1) Acetaldehyde butyl triethylsilyl acetal, preparation, properties, hydrolysis, 838.

2) Acetaldehyde isobutyl triethylsilyl acetal, preparation, properties, 838.

12. IV

$C_{12}H_{10}N_4Cl_5Sb$. Double diazonium salt, use in the synthesis of organoantimony compounds, preparation, decomposition in various solvents, and by various metals, 271.

$C_{12}H_{11}O_4N_2K$. Potassium salt of the monoenolate of 3-(3-acetylureido)-1-phenyl-1,2-propanedione, formation, 891.

$C_{12}H_{13}O_4N_2Br$. Product of Hofmann reaction with amide of N-acetyl-β-piperonyl-β-alanine, 465.

$C_{12}H_{28}O_4P_2S_4$. Disulfide obtained from O,O-diisopropyl hydrogen phosphorothiolothionate, 111.

12. V

$C_{12}H_{19}NPO_5Cl$. Hydrochloride of diethyl α-amino-3,4-methylenedioxybenzylphosphonate, preparation, 775.

$C_{12}H_{21}NPClO_3$. Hydrochloride of diethyl α-amino-p-methylbenzylphosphonate, preparation, 774.

$C_{12}H_{21}NPO_4Cl$. Hydrochloride of diethyl α-amino-p-methoxybenzylphosphonate, preparation, reaction with HCl, 775.

$C_{12}H_{21}NPClO_5$. Hydrochloride of diethyl α-amino-4-hydroxy-3-methoxybenzylphosphonate, preparation, reaction with HCl, 776.

$C_{12}H_{28}O_4P_2S_4Sb$. Lead bis(O,O-diisopropyl phosphorothiolonate), preparation, 111.

Group C_{13}

13. I

$C_{13}H_{18}$. 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphtalene, preparation, properties, condensation with maleic anhydride, citraconic anhydride, 2-methyl-2-cyclopenten-1-one, 2,4-dimethyl-2-cyclo-penten-1-one, 2-methyl-2-cyclohexen-1-one, 2-cyclohexen-1-one, 3,5-dimethyl-3-cyclopentene-1,2-dione, p-benzoquinone, 962.

13. II

$C_{13}H_8O$. Fluorenone, preparation, conversion to 9-methylfluorenol, 489.

$C_{13}H_9Li$. 9-Fluoroenyllithium, preparation, properties, 357.

$C_{13}H_{10}O$. 1,2-Dihydro-7-methoxy-4-vinylnaphthalene, preparation, properties, condensation with cyclic ketones to estrone derivatives, 982.

$C_{13}H_{12}O$. 4-Ethynyl-1,2-dihydro-7-methoxynaphthalene, preparation, properties, hydrogenation, condensation with 2-cyclopenten-1-one, 981.

$C_{13}H_{18}O$. 1-Ethinyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol, preparation, properties, exhaustive hydrogenation, 961.

$C_{13}H_{18}O_2$. 1) 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone, preparation, hydrogenation, splitting off acetylene, 76.

2) 8-Ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone, preparation, hydrogenation, 76.

$C_{13}H_{20}O$. 1) 1,2,3,4,4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol, preparation, properties, condensation with p-benzoquinone, 823.

2) 1,2,3,4,4a,5,8,8a-Octahydro-8a-methyl-1-vinyl-1-naphthol, preparation, properties, dehydration, 962.

3) Condensation product of acetone and 3-camphenilanecarboxaldehyde, formation, properties, semicarbazone, 729.

$C_{13}H_{20}O_2$. 1) Octahydro-5-hydroxy-4a-methyl-5-vinyl-2(1H)naphthalenone, preparation, dehydration, 77.

2) Octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone, preparation, dehydration, 77.

$C_{13}H_{22}O_2$. 1) 5-Ethyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone, preparation, 76.

2) 8-Ethyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone, preparation, 77.

3) Product of reduction of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone, 824.

$C_{13}H_{24}O$. 1-Ethyldecahydro-8a-methyl-1-naphthol, preparation, properties, 962.

$C_{13}H_{28}O_4$. 1) Bis-(isobutoxymethyl) ether of 1,2-propanediol, preparation, properties, 641; alcoholysis, 741.

2) Bis(butoxymethyl)ether of 1,3-propanediol, preparation, properties, 742.

3) Bis(isobutoxymethyl) ether of 1,3-propanediol, preparation, properties, alcoholysis, 742.

13. III

$C_{13}H_{13}NO$. 2,5-Dimethyl-1-phenyl-4-piperidone, preparation, hydrogenation, 275.

$C_{13}H_{19}ON$. Mixture of stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidinols, formation, hydrochloride, picrate, 278.

$C_{13}H_{22}ON_2$. 4-(2-Decalyl)-2-imidazolidinone, preparation, 235.

$C_{13}H_{21}ON$. 4-Ethynyldecahydro-1,2-dimethyl-4-quinolinol, preparation, solubility, picrate, 659.

$C_{13}H_{22}ON_2'$. Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninonitrile, preparation, cyanohydrin, 665.

$C_{13}H_{21}O_2N_3$. Semicarbazone of hexahydromethoxymethyl-1(2H)-naphthalenone, preparation, 75.

$C_{13}H_{23}ON$. Decahydro-1,2-dimethyl-4-vinyl-4-quinolinol, preparation, 660.

$C_{13}H_{23}O_2N$. β-(2-Decalyl)-β-alanine (β-amino-decahydro-2-naphthalenepropionic acid), preparation, properties, benzoyl derivative, 232.

$C_{13}H_{23}O_2N_3$. Octahydro-1(2H)-naphthalenone derivative semicarbazone, formation, 75.

$C_{13}H_{23}O_4N_3$. Product of reaction of hypobromite with ureide of 3-(ethoxycarbonylamino)-nonanoic acid 65.

$C_{13}H_{25}ON$. 4-Ethyldecahydro-1,2-dimethyl-4-quinolinol, preparation, picrate, 660.

$C_{13}H_{25}O_4N_3$. Ureide of 3-(ethoxycarbonylamino) nonanoic acid, preparation, action of hypobromite, 64.

$C_{13}H_{28}SiO_2$. Triethylsilyl heptanoate, preparation, properties, 122.

13. IV

$C_{13}H_{12}OPCl$. (Chloromethyl)diphenylphosphine, preparation, properties, 767.

$C_{13}H_{20}ONCl$. 2,5-Dimethyl-1-phenyl-4-piperidinol hydrochloride, formation, hydrogenation, 278.

Group C_{14}

14. I

$C_{14}H_{12}$. 1) 1,1-Diphenylethylene, preparation, dimerization, 487.

2) Diphenylethylene, polymerization, 991.

$C_{14}H_{14}$. Diphenylethane, chlorination, nitration, sulfonation, 481.

$C_{14}H_{20}$. 1) 1,2,4a,5,6,8a-Hexhahydro-4a-7-dimethyl-4-vinylnaphthalene, preparation, properties, condensation with 2-cyclohexen-1-one, 78.

2) 3,4,4a,7,8,8a-Hexahydro-6,8a-dimethyl-1-vinylnaphthalene, preparation, properties, condensation with 2-cyclohexen-1-one, 78.

14. II

$C_{14}H_{10}Cl_2$. Diphenyldichloroethylene, formation, 481.

$C_{14}H_{10}O_4$. Benzoyl peroxide, as catalyst in copolymerization of methacrylic acid and alkyl vinyl ethers, 934; reaction of bromoform and carbon tetrachloride with mercury in presence of, 595.

$C_{14}H_{12}O$. 9-Methylfluorenol, preparation, conversion to polydiphenylethylene, 489.

$C_{14}H_{22}O$. 1) 1,2,3,4,4a,7,8,8a-octahydro-2,4a-dimethyl-5-vinyl-2-naphthol, preparation, properties, dehydration, condensation with dimethyl maleate, 78.

2) 1,2,3,4,4a,7,8,8a-octahydro-2,8a-dimethyl-8-vinyl-2-naphthol, preparation, properties, dehydration, condensation with dimethyl maleate, 78.

3) Condensation product of 2-butanone and 3-camphenilanecarboxaldehyde, formation, properties, semicarbazone, 730.

4) Condensation product of ethyl acetate and 3-camphenilanecarboxaldehyde, formation, properties, 732.

$C_{14}H_{22}O_3$. Glycidic ester, preparation, reaction with potash, 232.

$C_{14}H_{22}O_8$. Acid diadipic ester of ethylene glycol, preparation, 849.

$C_{14}H_{26}O_4$. 1) Bis(butoxymethyl) ether of 2-butyne-1,4-diol, preparation, properties, 743.

2) Bis(isobutoxymethyl) ether of 2-butyne-1,4-diol, preparation, properties, 743.

3) Dibutyl adipate, reaction with ethylene glycol, 1,6-hexanediamine, 671.

$C_{14}H_{28}O$. Alcohol from reaction of Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene and 2,4-dimethyl-3-pentanone, formation, ozonization, dehydration, 910.

$C_{14}H_{30}O_4$. 1) Bis(butoxymethyl) ether of 1,3-butanediol, preparation, properties, 743.

2) Bis(iso-butoxymethyl) ether of 1,3-butanediol, preparation, properties, 743.

14. III

$C_{14}H_{11}O_5Cl$. 2-Methylnaphthopyranyl perchlorate, preparation, solubility, 431.

$C_{14}H_{12}O_4N_2$ Diacetyl derivative of 4-phenyl-2,5-pyrimidinediol, formation, 891.

$C_{14}H_{18}O_8N_4$. Picrate of 4-diethylamino-3-buten-2-one, formation, 885.

$C_{14}H_{21}ON_3$. 1) Semicarbazone of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone, preparation, 77.

2) Semicarbazone of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)naphthalenone, preparation, 77.

$C_{14}H_{23}ON$. 2-Methyl-4-ketoperhydro-6,7-(7,8)-benzoquinoline, preparation, properties, 452.

$C_{14}H_{23}ON_3$. Semicarbazone of condensation product of acetone and 3-camphenilanecarboxaldehyde, formation, 730.

$C_{14}H_{24}O_3N_2$. N-Carbamoyl-β-(2-decalyl)-β-alanine (decahydro-β-ureido-2-naphthalene propionic acid), preparation, action of HCl, 234.

$C_{14}H_{25}O_3N$. Methyl decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate, preparation, 666.

$C_{14}H_{30}ON_2$. Diamino ketone, preparation, properties, [1,5-bis(diethylamino)-3-hexanone], 290.

$C_{14}H_{32}O_2N_2$. Acetaldehyde bis[2-(diethylamino)ethyl] acetal, preparation, properties, 339.

14. IV

$C_{14}H_{11}OCl_4Fe$. 2-Methylnaphthopyranyl ferrichloride, preparation, solubility, degradation, conversion to perchlorate, 430.

$C_{14}H_{14}O_3NS$. Sulfone from aminobenzoyl derivative of 2,5-dimethyltetrahydro-1-thiopyran, preparation, 458.

$C_{14}H_{19}ONS$. Benzoyl derivative of 2,5-dimethyl-tetrahydro-1-thiopyran-4-amine, preparation, oxidation, 458.

14. V

$C_{14}H_{25}NPClO_3$. Hydrochloride of diethyl α-amino-p-isopropylbenzylphosphonate, preparation, reaction with HCl, 775.

Group C_{15}

15. I

$C_{15}H_{12}$. 1-Methylphenanthrene, preparation, properties, picrate, 963.

$C_{15}H_{14}$. 2-Methylphenanthrene, preparation, picrate, 79.

$C_{15}H_{16}$. 1,3-Diphenylpropane, preparation, 307.

15. II

$C_{15}H_{20}O_4$. Product of condensation of 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone with diethyloxalate, formation, 835.

$C_{15}H_{28}O$. Alcohol, formation, properties, 912.

$C_{15}H_{32}O_5$. Reaction product of sodium butoxide and the bis(chloromethyl) ether of ethylene glycol, formation, properties, 740.

15. III

$C_{15}H_{18}O_8N_4$. Picrate of 4-piperidino-3-buten-2-one, preparation, 885.

$C_{15}H_{21}O_2N$. Acetic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, hydrochloride, 282.

$C_{15}H_{22}N_2O$. Aphillidine, isolation from *Anabasis aphylla*, 471.

$C_{15}H_{23}ON$. 1) 4-(3-Buten-1-ynyl)decahyro-1,2-dimethyl-4-quinolinol, preparation, 661.

2) 4-Ethyl-2,5-dimethyl-1-phenyl-4-piperidinol, preparation, hydrochloride, 280.

$C_{15}H_{24}ON_2$. 1) (2-Decalyl)-dihyromethyl-4(3H)-pyrimidone, preparation, 233.

2) Aphilline, isolation from *Anabasis aphylla*, 471.

$C_{15}H_{25}ON$. 1,2-Dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline, preparation, properties, picrate, 452.

$C_{15}H_{25}ON_3$. Semicarbazone of condensation product of 2-butanone and 3-camphenilanecarboxaldehyde, formation, 730.

$C_{15}H_{25}O_2N$. Amino ketone, preparation, properties, 290.

$C_{15}H_{29}ON$. Amino ketone, preparation, properties, (5-dibutylamino-2-methyl-1-hexen-3-one), 290.

$C_{15}H_{29}ON$. 1) 4-Butyldecahydro-1,2-dimethyl-4-quinolinol, preparation, solubility, 661.

2) 1-Dibutylamino-5-methyl-4-hexen-3-one, preparation, properties, 291.

$C_{15}H_{31}ON$. 1-Dibutylamino-5-methyl-3-hexanone, preparation, properties, 291.

$C_{15}H_{32}Si_2O_4$. Bis(trimethylsilyl) azelaate, preparation, properties, 123.

15. IV

$C_{15}H_{20}ONCl$. 4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol hydrochloride, preparation, conversion to free base, hydrogenation, 279.

$C_{15}H_{22}O_2NCl$. Hydrochloride of the acetic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, conversion to free base, 282.

$C_{15}H_{24}ONCl$. Hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol, formation, 280.

15. V

$C_{15}H_{25}NPO_3Cl$. Hydrochloride of dibutyl α-amino-benzylphosphonate, preparation, properties, 774.

Group C_{16}

16. II

$C_{16}H_{24}O$. Condensation product of mesityl oxide with 3-camphenilanecarboxaldehyde, formation, properties, 731.

$C_{16}H_{24}O_3$. Condensation product of ethyl acetoacetate and 3-camphenilanecarboxaldehyde, formation, properties, semicarbazone, 732.

$C_{16}H_{28}O_2$. Formic ester of alcohol from reaction of Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene and ethylformate, hydrolysis, 911.

$C_{16}H_{30}O_5$. Acid ester of hexamethylene glycol and sebacic acid, formation 483.

16. III

$C_{16}H_{14}ON_2$. 3-Methyl-1,4-diphenyl-2-pyrazolin-5-one, preparation, properties, 594.

$C_{16}H_{23}ON$. Octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol, preparation, properties, 663.

$C_{16}H_{34}Si_2O_4$. Bis(triethylsilyl) succinate, preparation, properties, 123.

16. IV

$C_{16}H_{15}OCl_4Fe$. 2-n-Propylnaphthopyranyl ferrichloride, preparation, 431.
$C_{16}H_{15}OCl_4Fe$. 2-Isopropylnaphthopyranyl ferrichloride, preparation, 431.
$C_{16}H_{24}O_2NCl$. Hydrochloride of the propionic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, 282.

16. V

$C_{16}H_{27}O_5NPCl$. Hydrochloride of dibutyl *a*-amino-3,4-methylenedioxybenzylphosphonate, preparation, reaction with HCl, 775.
$C_{16}H_{36}O_4P_2S_4Hg$. Mercury bis(O,O-dibutyl phosphorothiolonate), preparation, 111.

Group C_{17}

17. I

$C_{17}H_{16}$. 2-Ethyl-1-methylphenanthrene, preparation, properties, 812, 833.
$C_{17}H_{28}$. 1) Polymerization product of 2,4,5-triisopropylstyrene, formation, 495.
2) 2,4,5-Triisopropylstyrene, preparation, polymerization, 494.

17. II

$C_{17}H_{15}N$. N-p-tolyl-2-naphthylamine, condensation with paraldehyde to form quaternary salts, 949.
$C_{17}H_{18}O$. 2,4,5-Triisopropylphenylmethylcarbinol, preparation, conversion to phenylurethane, 494.
$C_{17}H_{20}O_3$. Anhydride of 1,2,3,4b,5,8,8a,9,10a-decahydro-4b-methyl-1,2-phenanthrenedicarboxylic acid, preparation, 962.
$C_{17}H_{22}O_5$. 1) Condensation product of maleic anhydride and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone, formation, 78.
2) Condensation product of maleic anhydride and 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone, formation, 77.
$C_{17}H_{25}ON$. Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol, preparation, hydrochloride, picrate, 662.
$C_{17}H_{26}O$. 2,4,5-Triisopropylacetophenone, preparation, 493.

17. III

$C_{17}H_{14}O_2N_2$. Monobenzyl ether of 4-phenyl-2,5-pyrimidinediol, preparation, hydrolysis, 891.
$C_{17}H_{14}O_4N_2$. 1-N-Benzoyl-5-piperonylglyoxalidone, preparation, saponification, 463.
$C_{17}H_{16}O_4N_2$. Amide of N-benzoyl-β-piperonyl-β-alanine, preparation, Hofmann reaction, 462.
$C_{17}H_{17}O_2Br$. Ethyl bromo(phenyl)-p-tolylacetate reaction with mercury, 592.
$C_{17}H_{23}O_3N_3$. 5-(2-Benzamidooctyl)-1,3,4-oxadiazol-2(3H)-one, preparation, 63.

17. IV

$C_{17}H_{17}OCl_4Fe$. 2-Isobutylnaphthopyramyl ferrichloride, preparation, 431.
$C_{17}H_{21}N_4PO_{10}$. Picrate of diethyl *a*-aminobenzylphosphonate, preparation, properties, 774.
$C_{17}H_{26}O_2NCl$. Hydrochloride of the acetic ester of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol, preparation, 284.

Group C_{18}

18. I

$C_{18}H_{18}$. Hydrocarbon from steroid diketone, 811.

18. II

$C_{18}H_{15}Sb$. Triphenylstibine, preparation, dichloride, 273.
$C_{18}H_{20}O_2$. Methoxy ketone, preparation, reaction with methylmagnesium iodide, 982.
$C_{18}H_{22}O$. Condensation product of acetophenone and 3-camphenilanecarboxaldehyde, formation, properties, semicarbazone, 731.
$C_{18}H_{22}O_2$ Tetracyclic methoxy ketone, preparation, 982.
$C_{18}H_{22}O_3$. Anhydride formed from condensation of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene and citraconic anhydride, formation, hydrolysis, 962.
$C_{18}H_{22}O_4$. Tricyclic anhydride, from condensation of 3,4,4a,7,8,8a-hexahydro-4a-5-vinyl-2(1H)-naphthalenone, and citraconic anhydride, 823.
$C_{18}H_{24}O_2$. Isomers of 10-methyl-9-cardosterene-3,-15-dione, preparation, 835.
$C_{18}H_{24}O_4$. 1,2,3,4b,,8,8a,9,10,10a-decahydro-1,4a-dimethyl-1,2-phenanthrenedicarboxylic acid, preparation, dehydrogenation, decarboxylation, 963.
$C_{18}H_{28}O$. Condensation product of 3-camphenilanecarboxaldehyde and 6-methyl-5-hepten-2-one, preparation, properties, semicarbazone, 731.
$C_{18}H_{34}O$. Alcohol from reaction of amyl butyrate with the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene, formation, ozonization, 911.

18. III

$C_{18}H_{18}O_2N_4$. 2-(3-Acetylureidomethyl)-3-phenylquinoxaline, preparation, 892.
$C_{18}H_{23}ON_2$. 2,5-Dimethyl-4-phenyl-1-(2-pyridyl-4-piperidinol, preparation, hydrochloride, 281.
$C_{18}H_{25}O_2Br$. 1) (1)-Menthyl bromo(phenyl)acetate, reaction with mercury, 592.

2) (1)-Menthyl ester of bromo (phenyl)acetic acid, reaction with mercury, 594.

3) Diastereoisomeric (1)-menthyl esters of bromo(phenyl)acetic acid, preparation, properties, reaction with mercury, 585.

$C_{18}H_{25}O_2N$. Benzoic ester of decahydro-1,2-dimethyl-4-quinolinol, preparation, 665.

$C_{18}H_{27}ON$. Decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol, preparation, hydrochloride, 662.

$C_{18}H_{38}Si_2O_4$. Bis(triethylsilyl) adipate, preparation, properties, 123.

18. IV

$C_{18}H_{19}OCl_4Fe$. 2-n-Amylnaphthopyranyl ferrichloride, preparation, 431.

$C_{18}H_{23}ON_2Cl$. Hydrochloride of 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol, formation, conversion to base, 282.

$C_{18}H_{23}N_4PO_{10}$. Picrate of diethyl a-amino-p-phenylbenzylphosphonate, preparation, reaction with HCl, 774.

$C_{18}H_{25}O_2HgBr$. 1) (1)-Menthyl (bromomercuri) phenylacetate, preparation, properties, specific rotation, separation of (d) and (1) isomers, 585.

2) (1)-Menthyl (bromomercuri)-phenylacetate, preparation, 594.

Group C_{19}

19. I

$C_{19}H_{14}$. 2-Methylchrysene, formation, picrate, 79.

19. II

$C_{19}H_{18}O$. 16,17-Dihydro-3-methoxy-17-methyl-15H-cyclopenta[a]phenanthrene, preparation, 983.

$C_{19}H_{18}O$. Dehydrogenation product of steroid methoxy ketone, preparation, trinitrobenzene compound, 983.

$C_{19}H_{22}O_2$. 1) Mixture of steroid ketones, preparation, 984.

2) Steroid diketone. Condensation product of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene and p-benzoquinone, 967.

3) Steroid methoxy ketone mixture, preparation, dehydrogenation, hydrogenation, 983.

4) Steroid tetracyclic methoxy ketone, preparation hydrogenation, demethylation, 984.

$C_{19}H_{22}O_3$. Triketone, from condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone and p-benzoquinone, 823.

$C_{19}H_{24}O_2$. 1) Hydrogenation product of steroid methoxy ketones, mixture of isomers of methyl ether of estrone, 983.

2) Mixture of steroid methoxy ketones, preparation, 984.

3) Tetracyclic steroid methoxy ketone, preparation, demethylation, 984.

$C_{19}H_{26}O$. Steroid ketone, preparation, analysis, hydrogenation, 963; from condensation of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinyl-naphthalene and 2-cyclohexen-1-one, semicarbazone, 967.

$C_{19}H_{26}O_2$. 1) Isomers of 10,14-dimethyl-9-cardosterene-2,15-dione, preparation, isomerization, Clemmensen reduction, 834.

2) Steroid diketone, preparation, properties, isomers, 823; preparation, isomerization, Clemmensen reduction, 832.

$C_{19}H_{28}O$. 1) Reduction product of steroid diketone, formation, dinitrophenylhydrazone, dehydrogenation, 833.

2) Steroid ketone, preparation, hydrogenation, isomerization, 964.

$C_{19}H_{30}O$. Steroid ketone, preparation, 964.

19. III

$C_{19}H_{22}O_8N_4$. Picrate of 2,5-dimethyl-1-phenyl-4-piperidonol, formation, 278.

$C_{19}H_{23}ON$. 2,5-Dimethyl-1,4-diphenyl-4-piperidinol, preparation, hydrobromide, oxalate, hydrochloride, 281.

$C_{19}H_{24}O_4S$. Tetracyclic steroid diketo sulfone, preparation, 974.

$C_{19}H_{26}O_4S$. Tetracyclic steroid diketo sulfone, preparation, hydrogenation, 974.

$C_{19}H_{27}O_2N$. Acetic ester of the high melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol, preparation, hydrochloride, 664.

$C_{19}H_{30}O_4S$. Steroid tetracyclic diol, preparation, diacetic ester, oxidation, acetylation, 975.

$C_{19}H_{31}ON_3$. Semicarbazone of condensation product of 3-camphenilanecarboxaldehyde and 6-methyl-5-hepten-2-one, formation, 732.

19. IV

$C_{19}H_{24}ONBr$. Hydrobromide of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, formation, 281.

$C_{19}H_{24}ONCl$. Hydrochloride of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, formation, 281.

$C_{19}H_{28}O_2NCl$. Hydrochloride of acetic ester of the low-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol, preparation, 664.

Group C_{20}

20. I

$C_{20}H_{30}$. Hydrocarbon formed from steroid ketone, dehydrogenation, 965.

$C_{20}H_{32}$. Hydrocarbon from reduction of steroid diketone, 811.

20. II

$C_{20}H_{23}O_4$. 1) Dicarboxylic acid ester from condensation of dimethyl maleate with 1,2,3,4,4a,5,6,8a-octahydro-2,8a-dimethyl-8-vinyl-2-naphthol, formation, 79.

2) Dicarboxylic acid ester from condensation of dimethyl maleate with 1,2,3,4,4a,7,8,8a-octahydro-2,4a-dimethyl-5-vinyl-2-naphthol, formation, properties, 78.

$C_{20}H_{24}O_2$. Mixture of steroid methoxy ketones, preparation, demethylation, hydrogenation, 984.

$C_{20}H_{26}O_2$. 1) Mixture of steroid methoxy ketones, preparation, demethylation, 984.

2) Steroid diketone, from condensation of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene and 3,5-dimethy-3-cyclopentene-1,2-dione, formation, isomerization, 967.

$C_{20}H_{26}O_3$. Tetracyclic triketone, preparation, isomerization, 835.

$C_{20}H_{28}O$. Steroid ketone, preparation, hydrogenation, oxidation, Kizhner reduction, 964; preparation, semicarbazone, hydrogenation, 966.

$C_{20}H_{28}O_2$. 1) Steroid diketone, preparation, properties, isomers, Clemmensen reduction, 813; preparation, isomerization, Clemmensen reduction, 820; preparation, isomerization, reduction, 822.

2) Steroid diketone isomers, preparation, properties, Clemmensen reduction, 809.

$C_{20}H_{30}O$. 1 Hydrogenation product of steroid diketone, 810.

2) Ketone obtained by Clemmensen reduction of steroid diketone, action of methylmagnesium bromide and methyllithium, 822.

3) Steroid ketone, preparation, diodo compound, 965; preparation, 966.

$C_{20}H_{30}O_2$. Hydroxy ketone, preparation, properties, 812.

$C_{20}H_{30}O_4$. Dicarboxylic acid from ketone, 812.

$C_{20}H_{42}O_2$. 1,20-Eicosanediol, condensation with adipic acid, 849.

20. III

$C_{20}H_{22}O_4Hg$. Reaction product of ammonia and ethyl (bromomercuri) phenylacetate, 594.

$C_{20}H_{22}O_4N_2$. p-Nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, hydrochloride, 283.

$C_{20}H_{23}ON_3$. Semicarbazone of steroid ketone, formation, 967.

$C_{20}H_{23}O_2N$. Benzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, hydrochloride, 282.

$C_{20}H_{24}O_2N_2$. p-Aminobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, 284.

$C_{20}H_{24}N_2O_2$. Quinine, catalytic effect of, in the discharge of hydrogen ions in presence of amines, 715.

$C_{20}H_{25}O_2N$. Benzoic ester of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol, preparation, 665.

$C_{20}H_{26}O_2N_2$. 3-Benzoyl-4-(2-decalyl)-2-imidazolidinones, preparation, hydolysis, 234.

$C_{20}H_{26}O_3S$. Tetracyclic keto sulfone with a fluoreno [2,1-bc]thiapyran ring system, preparation; with phenanthro[2,1-bc]thiapyran ring system, preparation, 973.

$C_{20}H_{26}O_4S$. Tetracyclic diketo sulfone with phenanthro[2,1-bc]thiapyran ring system, preparation, isomers, 972; with fluoreno[2,1]bc]thiapyran ring system, preparation, 973.

$C_{20}H_{27}O_3N$. 1) Benzamido acid, preparation, 233.

2) N,N-Benzoyl-β-(2-decalyl)-β-alanine, preparation, reaction with thionyl chloride, 232.

$C_{20}H_{28}O_2N_2$. Isomeric amides of N-benzoyl-β-(2-decalyl)-β-alanine, preparation, hydrolysis action of acetic anhydride, 233.

$C_{20}H_{28}O_4S$. Tetracyclic steroid diketo sulfone, preparation, 974.

$C_{20}H_{29}O_2N_3$. Hydrazide of N-benzoyl-β-(2-decalyl)-β-alanine, preparation, 234.

$C_{20}H_{30}OI_2$. Diiodo compound of steroid ketone, preparation, 965.

$C_{20}H_{30}O_3S$. Tetracyclic steroid keto sulfone, preparation, 975.

20. IV

$C_{20}H_{23}O_4N_2Cl$. Hydrochloride of the p-nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, conversion to the free base, 283.

$C_{20}H_{24}O_2NCl$. Hydrochloride of the benzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol, preparation, conversion to free base, 283.

$C_{20}H_{26}ONCl$. Hydrochloride of 4-benzyl-2,5-dimethyl-1-phenyl-4-piperidinol, preparation, properties, 280.

$C_{20}H_{30}O_2NCl$. Propionic ester of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol hydrochloride, preparation, 664.

Group C_{21}

21. II

$C_{21}H_{21}Sb$. Tribenzylantimony, preparation, reaction with ethyllithium, 263.

$C_{21}H_{32}O$. Tetracyclic alcohol, reaction product of methylmagnesium bromide and steroid ketone, formation, dehydration, and dehydrogenation to chrysene, 967.

21. III

$C_{21}H_{18}NI$. 3-Methyl-4-p-tolylbenzo[f]-quinolinium iodide, preparation, reaction with ethyl orthoformate, and other compounds, 952.

$C_{21}H_{21}SiF$. Fluorotri-p-tolylsilane, preparation, properties, 761.

$C_{21}H_{22}O_4S$. Tetracyclic steroid methoxy keto sulfone, preparation, 974.

$C_{21}H_{29}O_4N$. Methyl-4-benzoyloxydecahydro-1,2,8a-trimethylcinchoninate, preparation, 666.

$C_{21}H_{31}ON$. Tetradecahydro-1,2-dimethyl-4-

phenylbenzo [g or h] quinolin-4-ol. preparation. 663.

$C_{21}H_{44}Si_2O_4$. Bis(triethylsilyl) azeleate. preparation, properties, 124.

21. IV

$C_{21}H_{26}O_2NCl$. Hydrochloride of the acetic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol. preparation, 285.

Group C_{22}

22. II

$C_{22}H_{40}O_4$. Eicosamethylene oxalate, polyester, formation, 995.

$C_{22}H_{42}O_6$. Dihexamethylene glycol ester of sebacic acid, formation, 483.

$C_{22}H_{46}O_{12}$. Product of reaction of ethyl vinyl ether with diethylene glycol, formation, properties, 94.

22. III

$C_{22}H_{31}O_3N$. Ethyl ester of N-benzoyl-β-(2-decalyl)-β-alanine, preparation, hydrazide, azide, 234.

$C_{22}H_{46}ON_2$. Diamino ketone. preparation, properties. [1,5-bis(dibutylamino)-3-hexanone] 291.

22. IV

$C_{22}H_{28}O_2NCl$. Hydrochloride of the propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol. preparation, conversion to the free base. 284.

Group C_{23}

23. II

$C_{23}H_{42}O_4$. Eicosamethylene malonate. polyester formation, 995.

23. III

$C_{23}H_{27}O_2N$. Propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, preparation, hydrochloride, 284.

$C_{23}H_{34}O_5S$. Diacetic ester of steroid tetracyclic diol, formation, 975.

Group C_{24}

24. II

$C_{24}H_{20}Si$. Tetraphenylsilane, preparation, 761.

$C_{24}H_{30}Si$. Dibutyl-1-naphthylphenylsilane, preparation, properties, 639.

$C_{24}H_{44}O_4$. Eicosamethylene succinate, polyester, formation, 995.

24. III

$C_{24}H_{38}O_6N_4$. Diacylhydrazine of 3-(ethoxycarbonylamino)nonanoic acid, preparation, 64.

$C_{24}H_{23}O_2N$. Phenylurethane of 2,4,5-triisopropylphenylmethylcarbinol. preparation, conversion to 2,4,5-triisopropylstyrene, 494.

Group C_{25}

25. II

$C_{25}H_{46}O_4$. Eicosamethylene glutarate, polyester, formation, 995.

25. III

$C_{25}H_{24}SiO$. Ethoxy-1-naphthylphenyl-p-tolylsilane, preparation, reaction with benzylchloride and magnesium. 640.

Group C_{26}

26. II

$C_{26}H_{42}Si$. 1-Naphthyldioctylsilane, formation, 639.

$C_{26}H_{46}O_8$. Acid ester of hexamethyleneglycol and sebacic acid, formation. 483.

$C_{26}H_{48}O_4$. Eicosamethylene adipate, polyester, formation. 995.

26. III

$C_{26}H_{27}O_2N$. Benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, preparation, hydrochloride. 284.

26. IV

$C_{26}H_{28}O_2NCl$. Hydrochloride of the benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, preparation, conversion to free base, 284.

Group C_{27}

27. II

$C_{27}H_{50}O_4$. Eicosamethylene pimelate, polyester, formation, 995.

Group C_{28}

28. I

$C_{28}H_{24}$. 1) 1-Methyl-1,3,3-triphenylindan, formation, 991.
2) 1,1,3,3-Tetraphenylcyclobutane, formation, 991.
3) 1,1,3-Triphenyl-3-methylhydrindene, formation, 487.
4) 1,1,3,3-Tetraphenyl-butene-1, formation, isomerization, 487; formation, 991.

28. II

$C_{28}H_{28}Si$. Tetra-p-tolylsilane, preparation, 761.

$C_{28}H_{52}O_4$. Eicosamethylene suberate, polyester, formation, 995.

Group C_{29}

29. II

$C_{29}H_{54}O_4$. Eicosamethylene azelate, polyester, formation, 995.

Group C_{30}

30. II

$C_{30}H_{56}O_4$. Eicosamethylene sebacate, polyester, formation. 995.

30. III

$C_{30}H_{27}N_2I$. 3-(p-Dimethylaminostyryl)-4-p-tolylbenzo-[f] quinolinium iodide, preparation, absorption maximum, 953.

30. IV

$C_{30}H_{25}N_2SI$. (4-p-Tolyl-3-benzo[f]quinoline)-(3-ethyl-2-benzothiazole)monomethinecyanine iodide, preparation, absorption maximum, 953.

Group C_{31}

31. II

$C_{31}H_{28}Si$. 1) 1-Naphthyl-tri-p-tolylsilane, preparation, properties, 640.
2) Tribenzyl-1-naphthylsilane, preparation, properties, 640.

Group C_{32}

32. II

$C_{32}H_{58}O_8$. Acid diadipic ester of 1,20-eicosanediol, preparation, 849.

32. IV

$C_{32}H_{27}N_2SI$. (4-p-Tolyl-3-benzo[f]quinoline)-(3-ethyl-3-benzothiazole trimethinecyanine iodide, preparation, absorption maximum, 952.

Group C_{33}

33. III

$C_{33}H_{27}N_2I$. (4-p-Tolyl-3-benzo[f]quinoline)-(1-methyl-4-quinoline)monomethinecyanine iodide, preparation, absorption maximum, 953.

Group C_{34}

34. III

$C_{34}H_{31}N_2I$. (4-p-Tolyl-3-benzo[f]quinoline)-(1,3,3-trimethyl-2-pseudoindole)-trimethinecyanine iodide, preparation, absorption maximum, 952.

Group C_{36}

36. III

$C_{36}H_{50}O_4Hg$. Diastereoismers of Di-(-)-menthyl ester of mercuribis[phenyl-acetic acid], preparation, properties, reaction with mercuric bromide, 758.

Group C_{40}

40. III

$C_{40}H_{48}N_2O_6$. Oxalate of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, formation. 281.

Group C_{43}

43. III

$C_{43}H_{33}N_2I$. Bis(4-p-tolyl-3-benzo[f]quinoline) trimethinecyanine iodide, preparation, absorption maximum, 952.

Group C_{50}

50. III

$C_{50}H_{92}O_{10}N_4$. Product of reaction of dibutyl adipate and 1,6-hexanediamine, 671.

ERRATUM

The following compound has been misplaced in this index of empirical formulas:

$C_{17}H_{25}ON$. Should appear under Group C_{17}, 17 III.
Appears under Group C_{17}, 17 II.

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PERIODICITY IN THE STRUCTURE OF THE ELECTRON ENVELOPES AND NUCLEI OF ATOMS*

COMMUNICATION 1. PERIODIC SYSTEM OF THE ELEMENTS AND ITS CONNECTION WITH THE THEORY OF NUMBERS AND WITH PHYSICOCHEMICAL ANALYSIS

A. F. Kapustinsky

1. Introduction

The fundamental law of chemistry — Mendeleev's periodic law — is manifested in a great variety of ways. It is most intimately bound up with the theory of atomic structure, and the periodic system of the elements derived from it consists in the classification of atoms according to the structures of their electron envelopes. The electronic theory of atomic structure and valency could not have developed, and cannot continue to develop, without the direct and determining participation of the Mendeleev law and the Mendeleev system. The question of the structure of the periodic system of the elements has been the subject of numerous investigations, which we have referred to in a series of communications [1,2,3]. In these communications we have considered, in a concise but sufficiently detailed fashion, the facts and principles that must find their expression in a modern scheme of the system of elements. In the present paper, in our considerations of the structure of the periodic system arrived at in this way, we shall confine ourselves to such exposition of the structure as is necessary for the comprehension of a treatment in which we throw further light on the system by the use of number theory and physicochemical analysis.

The use of mathematics as a means of generalizing data obtained by experiment, which is so characteristic of modern chemistry, does not replace real physicochemical objects by fictitious, abstract mathematical concepts. The object in our inferences here, and in other fields of science (for example, that of the phase rule) which are concerned with definite numerical relationships, is to represent facts observed by chemists by means of geometric models, and also to describe them with the aid of the language of mathematics. It is quite obvious that the systematization and description of known facts with the aid of mathematical terms and method cannot and does not lead to anything more than that which experiment yields to the investigator.

2. Structure of the Periodic System of the Elements

The rational structure of the periodic system of the elements contains: a) a zero period and zero group of elements; b) a subdivision of the system into even and odd periods and into cycles, which express a secondary periodicity; c) an evolutionary representation of the nature of the elements (proto-elements → typical elements → elements "of complete structure"). In Fig. 1 a stepwise representation of the system is given; in this the black spots represent elements of the even periods and circles represent those of the odd periods. The numbers of elements in the periods and in the cycles, each of which consists of a pair formed by an even and an odd period, are given below the diagram. The system is complete up to centium (z = 100). The same can be expressed by means of a network of cells (Fig. 2). The bold line represents a discontinuity; the cell occupied by hydrogen rests simultaneously on cells of groups I and VII. In the left part of the diagram the periods and cycles are given; and below the actinides and lanthanides are shown. The detailed derivation of these representations of the system, as also the arguments relating to the necessity of introducing the electron (e) and the neutron (n) into the system, is not given here (see [3]). We will add that in the table in Fig. 2 atomic weights are given and the recently discovered elements Athenium (An) and Centium (Ct) are included (as also in Fig. 1. The 6d shell is completed at element 104**.

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* Paper read at a conference held in Moscow in December, 1950, in commemoration of the founding, 30 years previously, of the D.I. Mendeleev Institute of Chemical Technology.

** Seaborg proposes to call it ekahafnium [4].

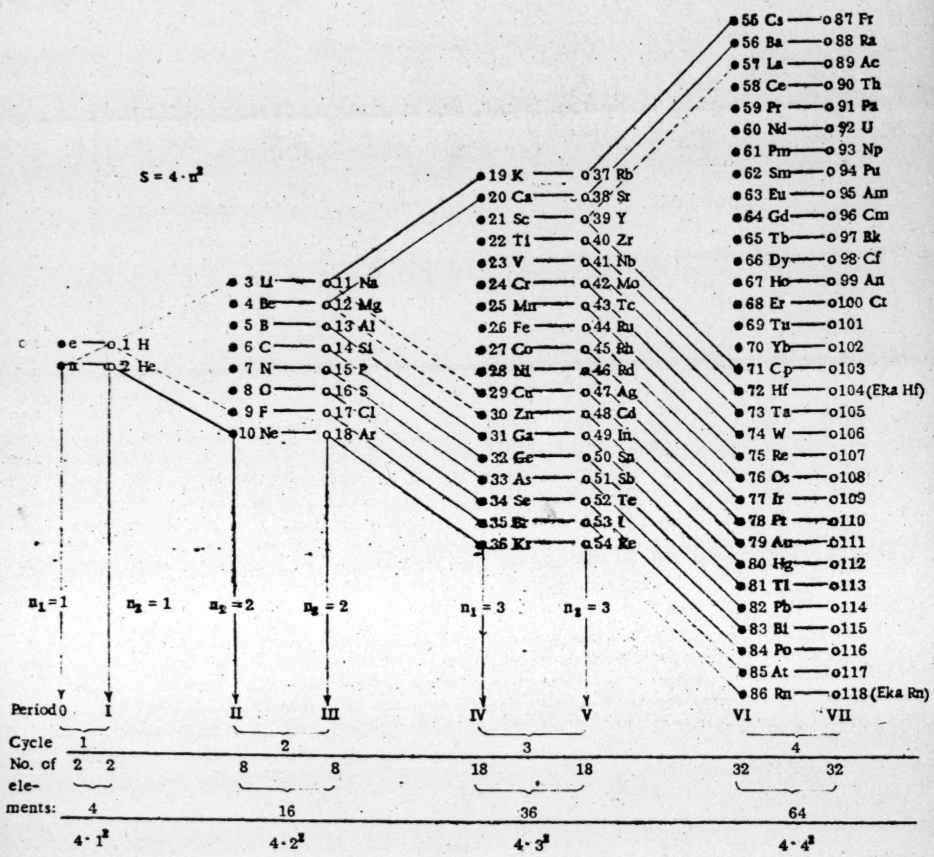
S = 4·n²
e — 1 H
n — 2 He
3 Li — 11 Na
4 Be — 12 Mg
5 B — 13 Al
6 C — 14 Si
7 N — 15 P
8 O — 16 S
9 F — 17 Cl
10 Ne — 18 Ar
19 K — 37 Rb
20 Ca — 38 Sr
21 Sc — 39 Y
22 Ti — 40 Zr
23 V — 41 Nb
24 Cr — 42 Mo
25 Mn — 43 Tc
26 Fe — 44 Ru
27 Co — 45 Rh
28 Ni — 46 Pd
29 Cu — 47 Ag
30 Zn — 48 Cd
31 Ga — 49 In
32 Ge — 50 Sn
33 As — 51 Sb
34 Se — 52 Te
35 Br — 53 I
36 Kr — 54 Xe
55 Cs — 87 Fr
56 Ba — 88 Ra
57 La — 89 Ac
58 Ce — 90 Th
59 Pr — 91 Pa
60 Nd — 92 U
61 Pm — 93 Np
62 Sm — 94 Pu
63 Eu — 95 Am
64 Gd — 96 Cm
65 Tb — 97 Bk
66 Dy — 98 Cf
67 Ho — 99 An
68 Er — 100 Ct
69 Tu — 101
70 Yb — 102
71 Cp — 103
72 Hf — 104 (Eka Hf)
73 Ta — 105
74 W — 106
75 Re — 107
76 Os — 108
77 Ir — 109
78 Pt — 110
79 Au — 111
80 Hg — 112
81 Tl — 113
82 Pb — 114
83 Bi — 115
84 Po — 116
85 At — 117
86 Rn — 118 (Eka Rn)
n₁ = 1
n₂ = 1
n₁ = 2
n₂ = 2
n₁ = 3
n₂ = 3
Period 0 I II III IV V VI VII
Cycle 1 2 3 4
No. of elements: 2 2 8 8 18 18 32 32
4 16 36 64
4·1² 4·2² 4·3² 4·4²

Fig. 1. Stepwise representation of the system

and at the end of the system is an atom of the inert-gas type belonging to the zero group, which it would be correct to call ekaradon (EkaRn). Altogether, there are 18 elements that have still not been discovered: from centium (100) to ekaradon (118). There can be no doubt that in their preparation, as also in their investigation, Mendeleev's law will play the same leading part as it has played up to the present.

3. Periodicity of the Properties of the Elements, and the Theory of Numbers.

There can be no doubt that it is in the theory of numbers that we find the best way of describing the periodic law and the periodic system in mathematical terms, for this branch of mathematics concerns itself with discontinuous quantities. Although Mendeleev pointed this out more than half a century ago [5], there have been no systematic attempts to apply the theory of numbers in chemistry.

D. I. MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

Cycle	Period	Series	GROUP										
			1	2	3	4	5	6	7	8			0
1	0	0				0 e							0 n 1.008
	1	I				1 H 1.008							2 He 4.003
2	2	II	3 Li 6.94	4 Be 9.013	5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00				10 Ne 20.183
	3	III	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.066	17 Cl 35.457				18 Ar 39.944
3	4	IV	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	
		V	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.6	33 As 74.91	34 Se 78.96	35 Br 79.916				36 Kr 83.7
	5	VI	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [99]	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	
		VII	47 Ag 107.88	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92				54 Xe 131.3
4	6	VIII	55 Cs 132.91	56 Ba 137.36	57 La •	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	
		IX	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po [210]	85 At [211]				86 Rn 222
	7	X	87 Fr 223	88 Ra 226.05	89 Ac • •								
		XI	—	—	—	—	—	—	—				118 Eka Rn

LANTHANIDES

57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm 147	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.9	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

ACTINIDES

89 Ac 227	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu [239]	95 Am [241]	96 Cm [242]	97 Bk	98 Cf	99 An	100 Ct	101	102	103

• Lanthanides • • Actinides

Fig. 2.

The use of mathematics in chemistry is possible on account of the correlation principle, which establishes the correspondence of mathematical forms and their transformations with physicochemical objects and the changes that they undergo. Therefore, we shall first establish corresponding chemical and mathematical concepts for examination. Kurnakov [6], in writing that "the law of constant and multiple proportions is an application of the study of whole numbers to chemistry", shared the views of Kummer [7], according to whom "chemistry and the theory of numbers have as their principle — although in different spheres of activity — the same concept of composition". Composition in chemistry is expressed with the aid of the concept of element, and an element is a form of material to which a definite place in Mendeleev's system corresponds. This definition is in complete accord with that proposed by Kedrov [8]: "an element is a species of atoms that occupy one definite place in Mendeleev's system".

In the system, the cell, which is denoted by a serial number (the atomic or Mendeleev number), is the element's "passport", characterizing its individual nature. Thus, to the number concept in mathematics there is a corresponding concept in chemistry of atomic, or cell number.

Among all the kinds of periodic relationships in chemistry, the most perfect and all-embracing is the system of elements. Can there be among the various mathematical functions one that could express the extremely high degree of organization and interrelationship of discontinuous quantities; that would have a dual character, expressing in itself the interaction of these quantities and the unity of their opposing characteristics; that would be constructed on the basis of the periodicity concept, not in the sense of simple repetitivity, but a concept of periodicity in its evolution at ever higher and higher levels, although in the form of an abstraction — a form that expresses in itself the transition from quantity to quality — a function that itself determines the composition of the groupings that arise ?

Number theory enables us to give an answer to this question. Let us suppose that we have the natural series of integers from 1 to 120 (the basis for the upper limit will be given later):

$$1,\ 2,\ 3,\ 4,\ 5,\ 6,\ 7,\ 8,\ 9 \ldots\ldots\ldots\ldots\ldots\ 120.$$

In this series particular sets of numbers show various forms of periodicity, as may be seen, for example, for the Bernoulli numbers; the repetitivity may vary greatly. Which of the possible solutions corresponds to the criteria given above ? We may first of all eliminate the variant of simple mechanical repetition, for the main requirement is the possibility of repetition that includes in itself evolution, i.e., that continually passes to a higher and higher level. This requirement corresponds to the next in order of reducing simplicity after the natural series: the series of squares of even numbers, 2^2, 4^2, 6^2, 8^2..., i.e., 4, 16, 36, 64,... We then have a periodicity of defined number cycles, which grow regularly as we move from the beginning of the series, thus satisfying the requirement given above.

The solution would remain incomplete if the concept of composition, so important from the chemist's point of view, were not expressed in it. According to the theory of numbers [9], every integer has at least two factors: itself and unity. A number having only two factors is prime, and one having more factors is composite. In the natural series of numbers 4 is the first and simplest composite number. Hence, the question of the composition of groupings of numbers developing cyclically in the natural series is equivalent to the question of repetitivity, in conformity with rule, of the simplest composite number, i.e., four, both as a beginning and as a basis. It has a simple and unequivocal solution, for the sets of numbers given above consist in an n^2-times repetition of four. In fact, every one of them is expressed by the formula $4 \cdot n^2$, where $\underline{n}$ is the number of the given grouping obtained by counting in order from the beginning of the system. Thus, the series of natural numbers contains growing cycles, each having $\underline{S}$ members and conforming to an extremely simple expression, which is not equivalent to other axioms, or theorems, and which is intimately bound up with the mathematical concept of composition, namely:

$$S = 4 \cdot n^2 .$$

By giving $\underline{n}$ the values 1, 2, 3, 4 we find that $\underline{S}$ becomes 4, 16, 36, 64. This expression is symmetrical and is in accord with the criterion of evenness and, in fact, duality.

The symmetry can be expressed by the condition stating that if the basis of the system is four, then its number of terms is also four. We then obtain a system of numbers:

$$4 \cdot 1^2 + 4 \cdot 2^2 + 4 \cdot 3^2 + 4 \cdot 4^2 = 120.$$

The evenness and dual character of this system permit us to break down each cycle into two halves. We have an analogous picture in a wave, which is composed of two half-waves. We shall call them number periods. According to definition, the number of numbers in the periods (which combine in pairs into cycles) will be (in order):

$$2,\ 2,\ 8,\ 8,\ 18,\ 18,\ 32,\ 32.$$

The system under consideration, therefore, forms itself into two number "rays" of periods — even and odd (according to the serial number of the period). Let us consider the results so obtained. With the aid of the theory of numbers and by an examination of the regularities found in the series of integers 1, 2, 3, 4, 5, 6 ......120, we conclude that within the limits of such a series:

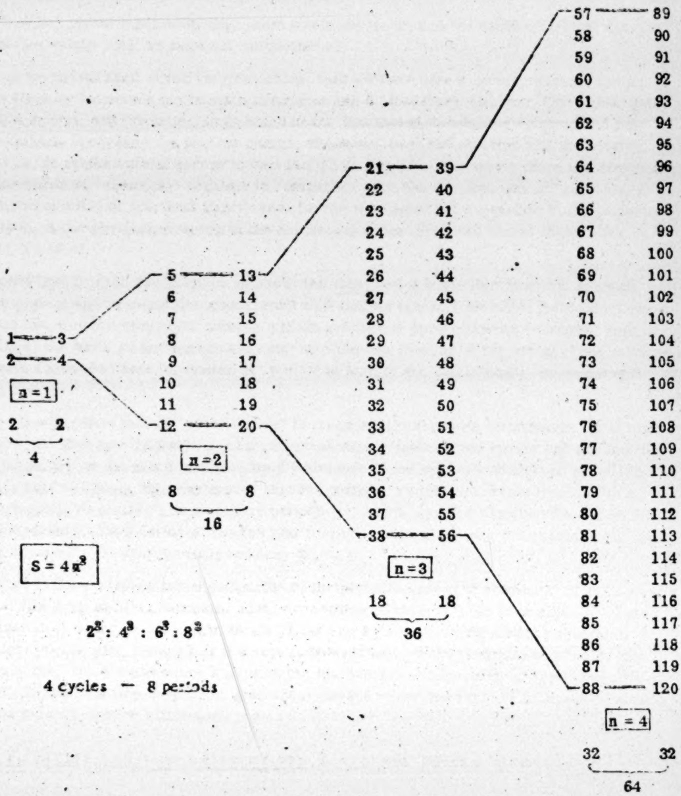
1 — 3
2 — 4
n = 1
2 2
4
5 — 13
6 14
7 15
8 16
9 17
10 18
11 19
12 — 20
n = 2
8 8
16
21 — 39
22 40
23 41
24 42
25 43
26 44
27 45
28 46
29 47
30 48
31 49
32 50
33 51
34 52
35 53
36 54
37 55
38 — 56
n = 3
18 18
36
57 — 89
58 90
59 91
60 92
61 93
62 94
63 95
64 96
65 97
66 98
67 99
68 100
69 101
70 102
71 103
72 104
73 105
74 106
75 107
76 108
77 109
78 110
79 111
80 112
81 113
82 114
83 115
84 116
85 117
86 118
87 119
88 — 120
n = 4
32 32
64
S = 4n²
2² : 4² : 6² : 8²
4 cycles — 8 periods

Fig. 3. Number system for n^2-times repetition of the simplest composite number.

a) there is a periodicity expressed by the set of numbers 1, 2, 3, 4, 5, 6 ....120;

b) the periods combine in pairs, each comprising an even and an uneven period, containing groupings of 4, 16, 36, 64, which conform to the law of an n^2-times repetition of the simplest composite number.

Such a mathematically derived concept of periodicity includes not only repetitivity of definite groupings (n^2-times repetition of the simplest composite number, four), but also the growth of cycles as they evolve; it expresses also the dual character and symmetry of structure of the system of numbers obtained — a structure formed by two — even and uneven — rays of periods. It is not difficult to see that we have satisfied all the requirements of a mathematical representation of the periodic system of the elements, the starting point for which is the correspondence between the concept of element in chemistry and that of number in mathematics, as formulated by us at the beginning. There only remains the final step of constructing a series of numbers from 1 to 120 following the results of the mathematical analysis of periodicity obtained above (Fig. 3).

A comparison of Figs. 1 and 3 confirms the complete identity of the periodic system of numbers with the variant we have developed of Mendeleev's periodic system. The structures of the two systems are identical. All parts of the two systems, in agreement with the correlation principle, correspond with one another: a) number —

element; b) "half-wave" or number period — period of the system of elements; c) number cycle — cycle of the system of elements, which combines within itself an even and an odd period.

It is obvious, of course, as we emphasized at the very beginning, that we have here a correspondence, not an identity. There is no simple equality between a mathematical number and a Mendeleev number. The former gives a formal ordinal number in the system, and the latter, in as much as the first two elements, the electron and neutron, have zero Mendeleev numbers, is equal to the nuclear charge. However, even the electron and the neutron, being individuals, correspond in the mathematical system to numbers (1 and 2). For this reason there is a displacement by two places in the succession of "chemical" numbers in comparison with the "mathematical" numbers, a circumstance that is without fundamental or practical significance for the mathematical expression of the periodic system of elements. What, then, is the physical meaning of the numbers that run like a red thread through the system under consideration, i.e., 2 and 4?.

First of all, it will be noted that 2 is the two possible values of the spin, and 4 is the four quantum numbers s, p, d, and f. But the most general and therefore the most correct explanation is that 2 expresses the dual character of the system of elements, and the simplest composite number 4 is the number of proto-elements (electron, neutron, proton, α-particle), which lie at the basis of the system and enter into the composition of the atoms of the remaining elements. All that we have expounded here, of course, is applicable both to the evolutionary and to the cell representation of the system.

The concept of "system" is wider than that of "periodic law" in its generally accepted formulation. It is true that a mathematical analysis of its structure indicates an exact correspondence between the system and the law of the periodic dependence of properties on the place occupied by the element in the system (Mendeleev periodicity), but that is not all. It emerges very strikingly from the system that the periods themselves, being repeated in a cyclic fashion, exhibit a "periodicity of periods", or secondary periodicity, which was first discovered by Biron [10]; it is not expressed at all in Mendeleev's formulation of the law and is closely associated with the general structure of the system in accord with the results of experimental chemistry [2].

What we have given above is not a mathematical derivation of the periodic system of elements. It is impossible to derive a real physical law from abstract numbers. Also, the correspondences that we have established are in no way intended as a replacement of the periodic law, in all its variety, by simple mathematical equations; they are intended to throw light on one part, although it is a very important part, of the problems relating to the structure of the system of elements. We are concerned only with the mathematical expression of experimentally found generalizations, but this is indeed a step toward the goal of Mendeleev — the discovery of an exact expression of the periodic law and of the periodic system of elements.

4. Physicochemical Analysis and Geometry of the Structure of the Mendeleev Periodic System of Elements

Graphical representation of various physicochemical systems and processes is widely used in general and physical chemistry. It has found its widest application in Kurnakov's physicochemical analysis, which brings together chemistry and geometry on the basis of correlation principles and of the continuity of transformations, and which enables us to make a new approach to the concept of the chemical individual.

It is possible that further development of the study of singular points in composition—property diagrams will reveal new methods for the graphical interpretation of Mendeleev's periodic law, in as much as the correspondence of any individual (daltonide) to a singular point coincides with the correspondence of an element — which is a chemical individual — to the concept of a special point in geometry. At the present time, however, at least without fundamental changes in the basic principles of physicochemical analysis, it is impossible to count on success in this direction.

The reason for this is that the method of physicochemical analysis, which can be successfully extended to any composition—property diagrams whatever, is strictly based on thermodynamical principles, as Kurnakov emphasized [6]. There is good reason why the main concept with which it operates should be the concept of a phase, homogeneous and continuous, as defined by classical thermodynamics. This is closely related to the fact that the principle of continuity of transformations occupies the foremost place in the theory of physicochemical analysis. The main laws, obtained in strict fashion by the use of above-described concepts, are extended further to non-equilibrium systems and non-thermodynamical properties.

However, neither the concept of the phase nor the principle of continuity of transformations is applicable to the analysis of the periodic system of the elements. In the first place, the periodic system is a system of atoms. It relates essentially to isolated atoms and also has no specific character such as is peculiar to statistical assemblies, i.e., phases, and is therefore like any generalization relating to the structures of atoms and molecules. In the second place, at least in the available range of temperature and pressure, there are no states of equilibrium and continuous transformations between the various elements; the periodic law cannot therefore be expressed with the aid of continuous functions. Hence, the geometry of the structure of the periodic system of elements must also be the geometry of discontinuity. Here lies the essential difference from the usually applicable methods of physico-chemical analysis. In all other respects, however, the ideas upon which Kurnakov based the theory of composition—property diagrams are quite applicable to the solution of the question of the geometrical representation of the structure of the periodic system of elements.

In accord with the correspondence principle, the concept of the element in discontinuous geometrical figures has its counterpart in the elementary square or cell. The next concept in complexity, the period, corresponds to a parallelogram (rectangle); the number of cells that it contains, which is equal to its area, is the number of elements in the period. Two contiguous periods (even and odd) taken together form a single cycle of the system. Thus, the geometrical counterpart of the cycle in the system of elements is the square, which is composed of two rectangles (right and left); its symmetry is expressed in its square outline, and the number of cells that it contains, which is equal to the number of elements, is therefore determined by the quadratic expression: $S = 4n^2$, where $\underline{n}$ is the series of integers.

C = 1

	0	1
P	e_0	1 H
A	n_0	2 He

C = 2

	2		3	
P	3 Li	7 N	11 Na	15 P
A	4 Be	8 O	12 Mg	16 S
P	5 B	9 F	13 Al	17 Cl
A	6 C	10 Ne	14 Si	18 Ar

C = 3

4			5			
19 K	25 Mn	31 Ga	37 Rb	43 Tc	49 In	P
20 Ca	26 Fe	32 Ge	38 Sr	44 Ru	50 Sn	A
21 Sc	27 Co	33 As	39 Y	45 Rh	51 Sb	P
22 Ti	28 Ni	34 Se	40 Zr	46 Pd	52 Te	A
23 V	29 Cu	35 Br	41 Nb	47 Ag	53 I	P
24 Cr	30 Zn	36 Kr	42 Mo	48 Cd	54 Xe	A

Fig. 4. Representations of cycles.

Starting from this correspondence of elements and structural parts of the periodic system with discontinuous geometrical forms, we can construct the corresponding representations for each of the cycles (Figures 4 and 5). In each square the cells corresponding to the elements are disposed in the order of the Mendeleev numbers of the elements. The "anisotropy" of each square consists in the fact that even and odd numbers (Mendeleev numbers) are brought together in alternative horizontal rows, thus bringing together Shchukarev's artiads and perissads [11] (denoted by A and P). Above each square the number of the cycle (C) is given, and above each rectangle, the number of the period.

It will be seen from the number of variables under examination that the system cannot be completely represented on a plane; it can be represented only in three-dimensional space. A three-dimensional figure containing squares in the form of sections parallel to the base separated by distances proportional to the capacities of the cycles is to be found in a truncated tetragonal pyramid (Fig. 6), which has a symmetry that is characteristic of the structure of Mendeleev's periodic system of elements and which consists of two halves, related symmetrically as mirror images, which are assigned to even and odd periods, respectively.

C = 4

6 7

P	55 Cs	63 Eu	71 Cp	79 Au	87 Fr	95 Am	103	111
A	56 Ba	64 Gd	72 Hf	80 Hg	88 Ra	96 Cm	104	112
P	57 La	65 Tb	73 Ta	81 Tl	89 Ac	97 Bk	105	113
A	58 Ce	66 Dy	74 W	82 Pb	90 Th	98 Cf	106	114
P	59 Pr	67 Ho	75 Re	83 Bi	91 Pa	99	107	115
A	60 Nd	68 Er	76 Os	84 Po	92 U	100	108	116
P	61 Pm	69 Tu	77 Ir	85 At	93 Np	101	109	117
A	62 Sm	70 Yb	78 Pt	86 Rn	94 Pu	102	110	118

Fig. 5. Representation of a cycle.

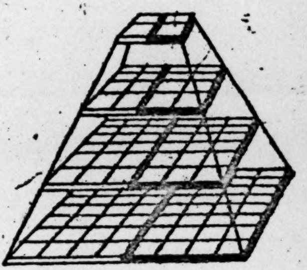

Fig. 6. Spatial representation of the system.

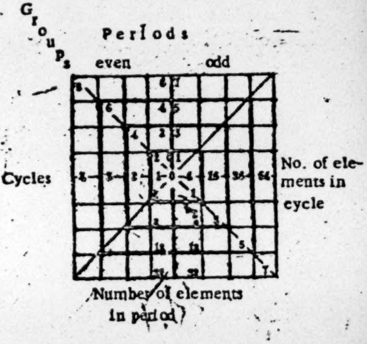

Fig. 7. Projection on the base of the spatial representation of the system.

This three-dimensional form of representation can be projected onto the base. The figure so obtained also presents a geometric expression of the structure of the periodic system of elements (Fig. 7). In the examination of this diagram, as also of the previous ones, it must be remembered that it is concerned with the geometric representation of the system and is not intended to replace in any way the evolutionary and tabular forms of the system (see Section 2).

In the geometric form given in Fig. 7, the interrelations of elements, periods, cycles, and (along the diagonal) groups are presented. The boundaries of the cycles are indicated by bold lines. All other indications are given directly on the figure. Such a diagram enables the interrelationship between all the concepts used in the construction of the periodic system to be represented in an extremely graphic fashion.

Just as, according to Kurnakov [6], any composition — property diagram is a closed complex, so in the diagram that we have advanced for the periodic system of the elements we find, using the word in the same sense, a closed diagram.

The geometric interpretation of the periodic system is in complete accord with the representation of the system in terms of number theory. "The system presents itself to us as a unified whole, harmoniously developed and having a regular and logical structure, answering in spirit and sense the designation "system"; its fundamental completeness is evident; it is incomplete only with respect to the discovery of new elements, in the effecting of which it will form, as it has done in the past, a leading thread in the investigations. All that we have expounded above will help in the realization of Mendeleev's goal: to give mathematical representations of the system with the aid of number theory and the geometry of discontinuous quantities.

SUMMARY

1. A horizontal, cell-form representation of the periodic system of elements is given in which

a) a zero period (electron, neutron) and zero group (neutron, He, Ar, Ne, Kr, Xe, Rn, ekaradon) are included;

b) subdivision is into periods and cycles expressing secondary periodicity;

c) there is a hydrogen "cell" adjoining Groups I and VII.

2. It has been shown that the structure of Mendeleev's periodic system can be described with the aid of number theory; and Kurnakov's physicochemical analysis is applied to the geometric representation of the periodic system.

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PERIODICITY IN THE STRUCTURE OF THE ELECTRON ENVELOPES AND NUCLEI OF ATOMS

COMMUNICATION 2. CLASSIFICATION OF THE ATOMIC NUCLEI OF THE ELEMENTS ON THE BASIS OF THE PACKING EFFECT AND THE LAYERED STRUCTURE OF THE ATOMIC NUCLEUS

A. F. Kapustinsky

1. Introduction

The exceptional progress made in the experimental chemistry and physics of the nucleus has not been accompanied by corresponding developments in the theory of nuclear structure. Although Ivanenko's proton-neutron theory is generally acknowledged, in detailed investigation recourse still has to be made to mutually inconsistent concepts, each of which is generally confined in its application to the solution of a special group of questions. Such nuclear models are: 1) those composed of independent particles, 2) similar to 1), but a closer approximation (Hartree), 3) those built from helions, 4) analogs of a solid, 5) analogs of a liquid drop. Fermi [1] has recently remarked that "different nuclear models give good descriptions of different peculiarities of the nucleus; no single one of the simple models accounts for all the properties of the nucleus". Jevons [2] also is not inclined to be optimistic; he asserts that "it may be said of many, if not of most, of the existing experimental data, that they are in very poor 'agreement' with theory". It would not be an exaggeration to assert that there is no general, single point of view consistent with the various experimental data to the extent found in the theory of electron envelopes of atoms. At the present stage of investigation — the stage concerned with the search for a general theory — it is useful, and even essential, to compare the various experimentally established properties of nuclei, to attempt to establish the quantitative relationships, even although they may be approximate, that are to be found, and to develop the corresponding schemes of classification and structural models — to do all, in fact, that can serve to further, widen, and intensify the investigation of this problem.

It must be said that this is indeed the direction followed in investigations by Spytsyn [3], Selinov [4], Sarkisov [5], Cherdyntsev [6], Znoiko [7], and others.

These investigations have revealed the undoubted existence of periodic relationships in the nucleus and have shown that the periodic properties may be of a most varied kind; the nuclear periodicities found, however, do not in any way form a simple repetition of the periodicity of the electron atmosphere.

In the present paper (see also Communication 1), we have tackled the problem of analyzing the possibility of the existence of a periodicity corresponding to a layered structure in the nucleus and of bringing it into relationship with Mendeleev's law.

2. Rectilinear-Diameter Rule for the Packing-Effect Curve

In the theory of atomic structure an essential part is played by the examination of the curve for the packing effect, which permits the relative stabilities of nuclei to be compared. This smooth curve, however, has not been subjected to a mathemetical analysis capable of relating together the characteristic quantities by which its position within the system of coordinates is determined: the packing effect $\underline{m}$, and the atomic number $\underline{z}$ (Fig. 1). However, by carrying out this analysis, we may, as will be shown below, not only relate this curve to analogous curves expressing other physicochemical functional relationships, but also arrive at certain generalizations essential to the classification of atoms.

Let us consider the most characteristic atoms for each element, namely, the isotopes that are most stable and most abundant in nature. It is to them, essentially, that our inferences will apply. Let us point out at once the exceptional position of beryllium, which, as Cherdyntsev emphasized [6], has, as its most abundant isotope, Be^9_4, in spite of the general rule of the greater abundance of even isotopes (abundance of Be^8_4 is 0.05 %).

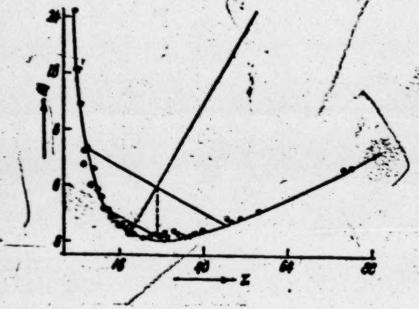

Fig. 1. Dependence of packing effect m on the atomic number z for the most abundant isotopes of the elements.

Fig. 1, which is constructed from compiled data [8], represents the relationship between the packing effect m and the atomic number (Mendeleev number) z, and not the mass number (the usual procedure). The evident symmetry of this curve prompted us to apply the method of analysis first developed for physicochemical curves of this type by Alekseev [9], who established the law of rectilinear diameter for the mutual solubility of liquids. A similar law was used by Cailletet and E. Mathias [10] for finding critical volumes.

We have drawn the curve in Fig. 1 so that its two branches are strictly symmetrical with respect to the rectilinear diameter passing through the vertex of the curve. The experimental values of the packing effect (Fig. 1) either coincide with the curve drawn in this way, or depart from it to an insignificant extent. We may remark that the departures are here less than for such classical examples of the application of the rule of rectilinear diameter as the systems carbon disulfide– methanol and triethylamine – water. Also, let us, following the custom for the rules of Alekseev – Cailletet – Mathias, call the lines perpendicular to the diameter and uniting corresponding points of the two branches of the curve by the name of connodes.

From an examination of Fig. 1 we come to the following conclusions:

a) The rectilinear diameter passes through a characteristic point, the vertex of the curve, corresponding to atomic number 20 (calcium). The isotope Ca$^{40}_{20}$ is characterized by the equality of the numbers of the three component parts of the atom: 20 electrons, 20 protons, 20 neutrons. This first characteristic point we shall call the critical point of the packing-effect curve.

b) The upper branch of the curve refers to atoms of elements standing before calcium in Mendeleev's system. Their general property is the equality in number of protons and neutrons; only for certain isotopes of maximum abundance (lithium, fluorine, sodium) is there an extra neutron. We shall call such atoms that are homogeneous with respect to number of protons and neutrons by the name of homonucleons, and the upper branch that corresponds to them – the homonucleon branch.

c) The lower branch refers to atoms of elements standing after calcium. For these, the further we go, the more the number of neutrons exceeds the number of protons. We shall call such heterogeneous atoms by the name of heteronucleons, and the corresponding section of the curve – the heteronucleon branch.

The above treatment enables us to arrive at a generalization, which may be called the rectilinear-diameter rule for the packing-effect curve (in coordinates of packing effect against atomic number): the packing-effect curve is a geometric locus of points equidistant from a rectilinear diameter passing through the critical point of the packing effect (Ca$^{40}_{20}$).

Another formulation of the rule, equivalent to the above, is as follows: the locus of the centers of connodes drawn through figurative points of the homonucleon and heteronucleon branches is a straight line passing through the critical point of the packing effect, z = 20 (Ca).

The equation of the rectilinear diameter for this case is:

$$\frac{m_1 + m_2}{2} = 0.85z - 22, \tag{1}$$

where m_1 and m_2 are corresponding figurative points (homonucleons and heteronucleons at the ends of the same connode).

Passing now to an examination of the electron envelopes of homonucleon atoms and heteronucleon atoms, we find that the atoms of all elements standing before calcium in Mendeleev's system have only s- and p-electrons, whereas those following calcium may have s-, p-, d-, and f-electrons. This may be represented as follows (Table 1):

TABLE 1

Nuclear characteristics	Homonucleons ←	Critical point of the packing-effect curve	Heteronucleons →
Electronic characteristics	s,p-electrons ←	Ca^{48}_{28}	s,p,d,f-electrons →

After an examination of the result obtained, it is impossible not to reach the conclusion that there is a definite correlation between the structure of the electron envelope and the type of nuclear composition.

We have considered the first characteristic point. We shall now show that the curve under analysis has a second characteristic point. Since the rectilinear diameter is not perpendicular to a coordinate axis, the packing-effect curve must have a minimum, at which the derivative of m with respect to z changes sign. We shall call the minimum point the second critical point of the packing-effect curve; its value may be found both directly from the graph (Fig. 1) and also by the aid of Equation 1. Actually, for the zero connode (i.e. that intersecting the zero level of the packing effect):

$$\frac{m_1 + m_2}{2} = 0 \tag{2}$$

Substituting from Equation 2 in Equation 1, we obtain the same result as that given directly by finding the minimum from the graph (Fig. 1), namely $z = 26$. This is the atomic number of the element corresponding to these minimum conditions, namely iron.

Among all the possible connodes there are two of particular significance: the zero connode $\frac{m_1 + m_2}{2} = 0$ just described, and the minimum connode, passing through the minimum of the curve ($z = 26$). They are not unrelated, on the contrary, as will be seen from the figure, they are related to one another: the perpendicular from the lower end of the minimum connode ($z = 26$) passes through the center of the zero connode. They form, therefore, a unified system. The four points corresponding to these connodes are special points on the packing effect curve; their values — $z = 6, 12, 26, 46$ — are the atomic numbers of carbon, magnesium, iron, and palladium. As is well known, one of the forms of expressing Mendeleev's periodic law is the curve of atomic volumes. It is these four elements that occupy the minimum positions on this curve; they are in the central positions in the corresponding periods of Mendeleev's system. We see that all four special points of the packing-effect curve belong to atoms of minimum volume in the periodic system, and since the atomic volumes are determined by the dimensions of the electron atmospheres of the nuclei, we again conclude that close correspondence must exist between the nuclear characteristics of an atom and the electron atmosphere of its nucleus.

3. Homonucleon and Heteronucleon Nuclei

The analysis that we have given of the packing-effect curve is only the first, rather crude approach to the solution of the general problem of the correspondence between the properties of the nucleus and of the electron envelope; it considers neither the question of even and odd atomic numbers, nor the finer points concerning the existence of isotopes, nor the tendency of atoms to undergo disintegration of various types. It permits us, however, to make a significant step forward, for it tells us of a quantitative relationship, the law of the rectilinear diameter, which brings the characteristic points of the packing-effect curve into relation with the minimum points of the curve of atomic volumes, and also brings nuclear characteristics into relation with the characteristics of the electronic atmosphere of the atom.

It is necessary to consider the division of the atoms of the predominating isotopes of the elements into homonucleons and heteronucleons in more detail. Although it is not of an absolute character (see, for example, Be^{9}_{4}), it gives a classification of elements that is correct in its main features from the point of view of the nucleon theory of the nucleus, and it again emphasizes the special part played by calcium (Ca^{48}_{28}).

From this point of view it is doubtful whether it is possible to draw a single curve having z and the ratio of the numbers of protons p and neutrons n as its coordinates. It would be more natural to regard it as consisting of two different branches: one relating to homonucleon elements, and the other to heteronucleons, the equation (3) established by Spitsyn [11]:

$$\frac{n}{p} = 1.13 + 0.057 \cdot z \qquad (3)$$

being regarded as applying to heteronucleons.

It is of interest to examine in greater detail the course of the changes in the numbers of protons and neutrons in the nucleus as the atomic number z increases. As will be seen from Fig. 2, this procedure gives only an approximate characterization of the atoms, which permits, however, the establishment of quite definite boundaries between various types of nuclei. In this figure, which is based on compiled data [12], the numbers of protons (p) and neutrons (n) in the nucleus are given on the axis of ordinates, and the number of protons (i.e. the atomic number z) on the axis of abscissas for the atoms of Mendeleev's system (the most abundant, the most stable, or those having the greatest half-life). With these coordinates curve 1 is, of course, a straight line (the proton line). The points on curve 2 represent numbers of neutrons. Here the division of nuclei into homonucleons and heteronucleons will be clearly seen. As is well known, the number of actinides is considered to be equal to the number of lanthanides, and the curves can be continued only to the supposed end of the Mendeleev system (p = 118). Fig. 2 (Curve 2) clearly indicates the presence of three breaks in the smooth course: around lithium and beryllium (p = 4), calcium (p = 20), and lanthanum (p = 56), which, according to the α-particle model, correspond to numbers of particles of 2, 10, 28, and 60 (at the end of the curve).

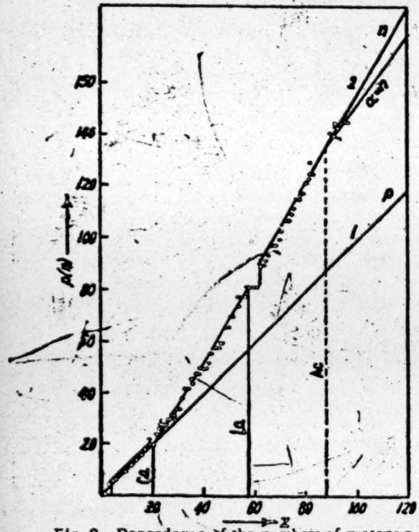

Fig. 2. Dependence of the numbers of protons p and neutrons n in the nucleus on the atomic numbers z of the most abundant isotopes

N	1	2	3	4
α	2	8	18	32
p	4	16	36	64

These breaks in the curves are not fortuitous and, in so far as we are concerned with nuclear properties, can be explained only by abrupt changes occurring in the structure of the nucleus in the course of its building up from nucleons. The following section of the paper is devoted to an attempt at such an explanation.

4. Periodicity in the Structure of the Nucleus Attributable to its Layered Structure

In the explanation of various properties of atoms, particularly in isotype chemistry, the most useful theory has been the α-particle hypothesis of nuclear structure, first stated by Rutherford in 1927 and later developed in various directions by Cherdyntsev [6], Spitsyn [13], Gapon [14], Sarkisov [5], and other investigators. Starting from the basic ideas of this theory and regarding the α-particles in the nucleus as single particles formed by pairs of neutrons and protons, we may explain the breaks in the curve in Fig. 2 with the aid of the following hypothesis of the layered structure of the nucleus.

The so-called "Pauli exclusion principle", formulated in the first place with respect to electrons and later extended also to nucleons, was found to be inapplicable to α-particles, as also was Fermi statistics. Even if another method of theoretical physics is developed in the future which will permit the application of this principle to helions, or even if it is formulated in somewhat different form, there is still an evident need for the development of a theoretical method for the "selection" of particles according to their energy characteristics. It is of interest to attempt to apply this principle in its simple, non-complicated form to the classification of helions. If we postulate that α-particles play the part of single particles in the nucleus and have energy characteristics given by a set of four quantum numbers, analogous to the quantum numbers of electron chemistry, we arrive at results that are in good agreement with the facts presented graphically in Fig. 2.

If we assume that an exclusion principle analogous to that for electrons and nucleons is extended also to α-particles, we are in fact asserting that there cannot be two helions in the nucleus having identical sets of four energy (quantum) characteristics. Calculating, in the manner usual in quantum theory, the number of possible groupings in each layer ("quantum level"), we obtain (see Table 2) the numbers of α-particles in the first, second, third, and fourth layers, the resulting values being 2, 8, 18, and 32, corresponding to total numbers of helions of 2, 10, 28, and 60, or to numbers of protons of 4, 20, 56, and 120, which coincide exactly with the atomic numbers of the elements corresponding to the breaks in Fig. 2* (Table 2).

Thus, the hypothesis of a layered helion structure is satisfactorily supported by the facts. It will be evident that nuclei have a four-layer structure: in the first layer there cannot be more than 2 α-particles; in the second — not more than 8; in the third — not more than 18; and in the fourth — not more than 32.

TABLE 2

Quantum level	1	2	3	4
Number of α-particles in each layer	2	8	18	32
Total number of α-particles in nucleus	2	10	28	60
Total number of protons in the nucleus	4	20	56	120
Number of protons in nucleus corresponding to the breaks in the curve in Fig. 2	4	20	56	(120)
Number of protons in each layer	4	16	36	64

The layered nature of the nucleus is determined by its helion composition; the α-particles constitute, as it were, a "skeleton", the structure of which mainly determines the structure of the nucleus. The neutrons evidently play the part of binding particles, cementing the helions together. As a result of the rapid growth of their number, already in actinium they become equal in number to the α-particles. It is possible that a structure then arises, similar to that of NaCl crystals, in which α and n alternating checkerwise in space, evenly and compactly fill the given volume. Such an arrangement is a limiting one: further increase in the "concentration" of neutrons renders the nucleus unstable. This feature, in fact, is characteristic of the transuranides (actinides). It may be considered that beyond the boundary indicated by the broken line in Fig. 2 an inflection will occur in the Curve 2, which will proceed as shown for $\alpha = n$. The tendency for the further accumulation of neutrons leads to a boundary at p = 118 at the end of the periodic system, and beyond this the existence of nuclei becomes energetically impossible. This does not, of course, exclude the existence of other, more complex forms of matter, for example, complex polynuclear formations analogous to polynuclear coordination compounds in the chemistry of complex compounds. But these stand outside the framework of the periodic system of the elements.

Although we find a layer in the structure of the nucleus corresponding to the lanthanides in the structure of the atom, the actinides do not correspond to the formation of a special layer, but to the onset of a condition of non-equilibrium between α-particles and neutrons. The analogy between lanthanides and actinides, therefore, is incomplete, being the result of different causes. In fact, whereas the former are stable, the latter are characterized by unstable nuclei.

Here we again arrive at interesting comparisons between the structure of the nucleus and that of the electron atmosphere. In just the same way as the electron atmospheres of inert-gas atoms consist of complete stable layers, we have also complete stable layers of helions in the nucleus (Fig. 3). The number of protons in these layers corresponds to the number of elements in paired groupings (cycles) of Mendeleev's system (4, 16, 36, 64), and the number of α-particles that they contain corresponds to the number of elements in the periods (2, 8, 18, 32). The last question will be considered in the next section.

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* An examination of the isotopic compositions of elements prompted Bethe and Bacher [15], and later Mayer, Nordheim, Haxel, and others, to suggest the presence of a series of closed proton — neutron shells in the nucleus. This suggestion will not be considered here, for their hypothesis of the presence of proton — neutron groupings in the nucleus containing 20, 50, 82, and 126 particles does not appear to have a sufficient basis and does not permit the systematic development of a theory of zonal nuclear structure directly related to the theory of the electron atmosphere of the atom. References to the literature on this question have been given by Duckworth [16].

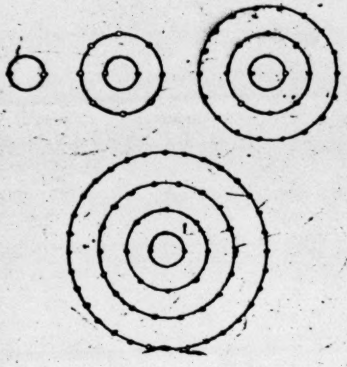

Fig. 3. Periodic (layered) model of the atomic nucleus. The filling of the first, second, third, and fourth layers by α-particles.

5. Relation of Nuclear Structure with the Structure of the Electron Envelopes of Atoms

This section is devoted to the question of the correspondence between the structure of the electron envelopes of atoms and the structure of the atomic nucleus. We shall compare the cycles and periods of Mendeleev's system, which are determined by the layered arrangement of electrons in the atom, with the periods of the nucleus, which are determined by the number of helions (and also by the number of protons entering into their composition) in each layer of the nucleus. Table 3 gives the number of elements (which is equal to the number of electrons, since the atomic number is equal to the number of electrons in the atom) and the number of protons in the nuclear layer for each cycle (cf. Table 2).

TABLE 3

Cycle	1	2	3	4
No. of elements in cycle (No. of electrons)	4	16	36	64
Number of protons in the layer of the nucleus	4	16	36	64

The correspondence is so complete that comment would be superfluous. The cyclic character of Mendeleev's system of elements corresponds to the cyclic character found in atomic nuclei: 4 layers in the nucleus — 4 cycles in the system.

We shall compare now the number of elements in a period with the number of helions in each layer of the nucleus (Table 4).

TABLE 4

Periods	0 and 1	2 and 3	4 and 5	6 and 7
Number of elements in period	2 and 2	8 and 8	18 and 18	32 and 32
Number of helions in a layer of the nucleus	2	8	18	32

We see that each even and odd period contains a number of elements equal to the number of helions in a period of the nucleus. The results of these comparisons may be formulated as follows:

1. The cycles of Mendeleev's system of elements correspond to layers (cycles) of the nucleus, and the number of elements (electrons) in a cycle is equal to the number of protons in each helion layer of the nucleus.

2. The periods of Mendeleev's system are determined in pairs by the number of helions in a layer of the nucleus.

There can be no doubt, therefore, in the following inference: the structure of the periodic system of elements, and therefore also the layered arrangement of electrons in the atom, stands in an exact, clear relationship with the structure of the system of atomic nuclei, with the layered arrangement of particles entering into the composition of the nucleus. It is possible that the structure of the electron atmosphere of the atom is determined mainly by nuclear forces, i.e., is determined by the structure of the nucleus.

Attention must be drawn to a characteristic peculiarity of the periodicity of the nucleus, which results from the fact that the composition of the nucleus differs essentially from that of the envelopes of atoms. Periodicity in Mendeleev's system is mainly the result of periodicity in the electron atmosphere, for it is on this that the chemical properties depend. Elements having electron atmospheres, however, begin only with hydrogen, i.e., they are delayed to the extent of two places (a zero period) behind the beginning of the system. This is the reason for there being only a correspondence and not an identity in the characteristics of the periodicity of the nucleus and its atmosphere: "chemical" (electronic) periods and cycles begin always two places earlier than those in the nucleus. For example, that which occurs for Ne_{10} is repeated for Ca_{20} the previous layer of electrons ends at Ar_{18}, and only after two places does the completion of the helion layer occur (at Ca^{40}_{20}), after which a new layer begins in the nucleus *. The same occurs further on: Ba_{56}, standing two places after Xe_{54}, is the boundary for the completion of the third layer of helions in the nucleus.

The internucleon forces in the nucleus are very powerful, and greatly exceed the weaker interactions that rule outside the nucleus. In the nucleus, therefore, we do not have incomplete levels and the completion of these levels. These finer nuances exist only in the electron atmosphere of the atom; they are peculiar to it, and there is evidently nothing that corresponds among the structural peculiarities of nuclei. This question, however, must be the subject of further investigation.

SUMMARY

1. A rectilinear-diameter rule is proposed for the packing-effect curve. It states that this curve is the locus of points equidistant from a rectilinear diameter passing through the critical point of the packing effect (Ca^{40}_{20}). The equation for the rectilinear diameter in terms of the atomic number is given. It is shown that the characteristic points determining the position of the packing-effect curve coincide with the minimum points of the atomic-volume curve.

2. With the aid of concepts of homonucleon nuclei (equal numbers of protons and neutrons) and heteronucleon nuclei (number of neutrons exceeds number of protons), the correspondence between the compositions of the nucleus and of its electron atmosphere is examined.

3. On the basis of an examination of the breaks in continuity on the diagram of number of nucleons plotted against atomic number, a hypothesis is advanced concerning the layered structure of the nucleus, the maximum number of helions in the layers being 2, 8, 18, and 36.

An attempt has been made to extend the "exclusion principle" to the helion model of the nucleus, in order to explain the existence of four layers of helions in the nucleus.

4. It has been established that a correspondence exists between the four cycles of Mendeleev's system of elements and the four layers in the structure of the nucleus and between the number of elements in the periods and the number of protons (entering into the composition of the helions) in the layers of nuclei. The periodicity in the structure of the electron envelopes is brought into relationship with that of the layers in the atomic nucleus.

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* It is interesting to note that the existence in the nucleus of a closed shell containing 20 neutrons and 20 protons (Ca^{40}_{20}) is predicted also by Hartree's method, as was shown by Wiegner and Barkas [17].

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DETERMINATION OF THE STRUCTURE AND STRUCTURAL FORMULAS OF ORGANIC COMPOUNDS FROM CRYSTALLOGRAPHIC DATA

G. B. Boky

1. There are a number of well known difficulties which the theory of the structure of organic substances has met in the field of aromatic compounds. For example, by the use of Kekulé's model of the benzene nucleus it was found to be impossible to explain the absence of two ortho isomers among benzene derivatives and to dispose single and double bonds in a rational fashion in a whole series of aromatic compounds having condensed nuclei. As a result of these difficulties, organic chemists went to the other extreme and abandoned attempts to give exact representations of formulas by the aid of valency lines. In textbooks and scientific literature benzene rings began to be represented by simple hexagons, without any indication of the distribution of single and double bonds. This "leveling out" of bonds amounted to the recognition in benzene nuclei of only one type of bond between carbon atoms — intermediate between single and double.

If we employ the elementary electronic concepts widely used in organic chemistry and assign three valency electrons to each such bond, we can obtain a scheme for the structure of the benzene molecule. This scheme, however, cannot be used for representing the structures of naphthalene, anthracene, and other more complex substances. In the naphthalene molecule, for example, there are 11 bonds between carbon atoms, but the number of valency electrons remaining for their formation is 32.

The "leveling out" of all the bonds between carbon atoms in aromatic compounds is in conflict also with a number of recent experimental results on interatomic distances and the symmetry of organic compounds. These data are published mainly in special crystallographic journals, and often remain unknown to the majority of organic chemists.

2. The present stage of development in chemistry is associated with the appearance of the method of x-ray-structure analysis, which enables us to determine interatomic distances in molecules and radicals and thus introduce a quantitative element into the purely qualitative stereochemical concepts of classical chemistry. This demands consideration of the values of interatomic distances and, in particular, their influence on the chemical behavior of molecules.

It is impossible, however, to approach this question in a purely mechanical fashion and consider that each valency line in the formula always corresponds to the same interatomic distance in the structure of an organic compound. The mutual effects of atoms in molecules may bring about substantial changes in interatomic distances. The lengths of bonds between carbon atoms (or atoms of other elements) of identical multiplicity may have different values in different compounds, and even in one compound between different atoms. The length, however, of the bond between corresponding atoms in different crystals of the same compound has always a quite definite value.

First of all we shall consider the effect due to changes in valency angles. In 1944, when carrying out an analysis of the structure of PtS, we pointed out that, in spite of the great difference in electronic structure between platinum and sulfur atoms and the difference in the values and spatial arrangement of the valency angles, their deformations are approximately the same [1]. Kitaigorodsky had demonstrated the same idea with respect to pairs of molecules such as $CHCl_3$, CH_3Cl, and others having strictly tetrahedral valency angles.

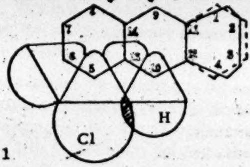


Fig. 1

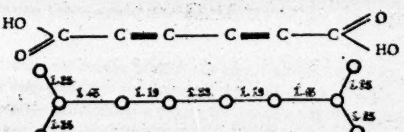


Fig. 2.

In Fig. 1, the hydrogen and chlorine atoms are drawn to scale. The repulsion of chlorine and hydrogen atoms not united by a valency (at 5— and 10—C) is bound to result in the lengthening of the 10—13 bond.

The distortion effect in the valency angles will evidently be more marked at the edges of molecules and may therefore be called the "edge effect". Atom 1 will be repelled from atom 9, since it meets no resistance from the opposite side (see Fig. 1); this will lead to lengthening of the bond 1 − 11 and shortening of the bond 1 − 2, accompanied by increase in angles 2 and 3 to values above 120° and decrease in angles 11 and 12. Shortening of the bond between atoms 1 and 2 may lead to the localization in this place of a double bond and therefore further reduction in the distance between these atoms.

The occurrence of single bonds between multiple bonds leads, as is well known, to their shortening. This effect is very much more marked than the interatomic-distance effects observed for atoms not united by valency. In particular, it has long been known that in paraffins and other aliphatic compounds a single bond has a length of the order of 1.54 A, or even somewhat greater than this. In aromatic compounds, however, the length of a single bond is not generally greater than 1.45 − 1.46 A. As an example of very considerable shortening of a single bond let us examine the results of the X-ray analysis of the dihydrate of butadiynedicarboxylic acid (Fig. 2) [2].

The distance between carbon atoms in the system $\equiv C-C\equiv$ is 1.33 A, instead of the usual 1.54 A in paraffins. It is less than the usual distance for a double bond C=C (about 1.35 A). This example shows that the length of a bond is not always an unequivocal characteristic of its multiplicity. Naturally, the properties of the bond will change also, if its multiplicity is maintained but its length considerably altered. Sometimes bonds of equal length must be assigned differing multiplicities, and in special cases it is conceivable that the shorter bond may have a lower degree of multiplicity. These, of course, are exceptional cases. In the general case, however, other things being equal, shorter interatomic distances correspond to higher multiplicity in the bond. The same interatomic distance of about 1.4 A may, however, correspond either to a double or to a single bond.

3. In order that all the available experimental material on interatomic distances in organic molecules may be in agreement with Butlerov's theory of structure, it is necessary to make the assumption, which has been suggested previously on several occasions, of the possibility of the existence in aromatic compounds not only of single and double bonds, but also of intermediate, "one-and-a-half fold" bonds, indicated in the schemes that follow by the sign .\ We shall not consider the nature of this bond in this paper. The object of our work here is quite different: we shall try to show the mutual effect of atoms and the possibility of representing any molecule by a single structural formula. The latter, of course, is possible only when there are experimental data of sufficient accuracy regarding the interatomic distances. For the representation of structural formulas of aromatic compounds, it is sufficient to use bonds of three types: single, double, and 1.5 - fold. Other things being equal, atoms bound by a distance intermediate between the distances appropriate for a single and for a double bond.

Kekulé's hypothesis contemplated the existence in aromatic compounds of carbon atoms of only one type $>C=$; we shall call this type A. The hypothesis stated above contemplates the existence of atoms not only of Type A, but also of a second type $>C\underset{\cdot}{-}$; we shall call this Type B. In checking these ideas against the experimental material, we shall take the idea of the preservation of a definite symmetry in the molecules as our basis.

In studying the symmetry of large ions and of molecules of complex compounds, we concluded that in entering into the crystal such polyatomic structural units lose their symmetry according to a definite succession: high-order axes are lost most readily of all, then the planes, and finally the center, of symmetry [3]. If there is a center of symmetry in a complex ion or molecule, then it is generally preserved when the ion or molecule enters a crystal. This rule must hold all the more for organic compounds, for intermolecular forces (which are the main cause of the loss in symmetry of molecules on entering into crystals) are considerably weaker in organic than in inorganic compounds.

4. Let us examine the structure of the naphthalene molecule on the basis of the above discussion. Two "equivalent" structural formulas (I and II), having different dispositions of the double bonds, are given in textbooks for naphthalene (Fig. 3). The interatomic distances and the presence of a center of symmetry in the naphthalene molecule (III) [4] definitely indicates the superiority of structural formula II over I. The difference in distances between carbon atoms linked with like bonds . . . . C = C . . . . . = 1.37 A ± 0.02 and . . . C − C. . . = 1.41 A ± 0.02 lies almost within the limits of experimental error. The central double bond is somewhat longer than the average double bond, and the outer single bonds are somewhat shorter than usual. This is what determines their equality in length.

The structure of the 15-dichloronaphthalene (IV, Fig. 3, Kitaigorodsky and Kobalkina [5]) confirms, even better than the structure of the naphthalene molecule, the same localization of double bonds.

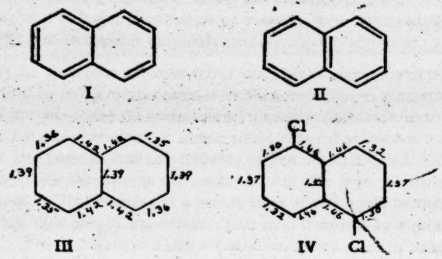


Fig. 3.

Unsurmountable difficulties are met in attempts to determine the disposition of double bonds in the anthracene molecule, if Kekulé's formula for benzene is used. Neither of the variants I and II (Fig. 4) can be reconciled with the existence of a center of symmetry in the anthracene molecule (III), which is definitely shown to exist by the X-ray investigations of Sinclair, Robertson, and Mathieson [6]. The same data, however, are in good agreement with the structural formula IV, constructed of carbon atoms of Type B. The distances between atoms linked by 1.5-fold bonds are each 1.39 ± 0.03 A. Replacement in the 1 5-positions of hydrogen by chlorine preserves the center of symmetry of the molecule (V), but leads to a rearrangement of bonds (VI) [5]. The increase in the two C–C distances (V) to 1.45 A in the central hexagon is associated with the repulsion of these hydrogen atoms from the chlorine atoms.

A different regrouping of bonds in the anthracene molecule is to be observed when oxygen is introduced in the 9- and 10-positions. The interatomic distances (according to Sen [7]) in the anthraquinone molecule are shown in Fig. 4 (VII). The distribution of bonds is shown in formula VIII. The oxygen atoms are here bound by double bonds. The distance . . . . . . C=O . . . is 1.15 A. In carboxyl groups, however, the bonds between oxygen and carbon are identical ([2], see Fig. 2) and are evidently 1.5-fold, which should be indicated in the formula by the corresponding sign. The distance ...C–O is 1.25 A. In a single bond the ..C−O.. distance rises to 1.4 A or higher.

Returning to the structure of anthracene and its derivatives, we may note that, according to the type and position of a substituent, the numbers of carbon atoms of Type A and Type B may change considerably. Thus in anthracene all the carbon atoms are of Type B (Fig. 4). In 1,5-dichloroanthracene 8 carbon atoms are of Type A and 6 atoms are of Type B. In anthraquinone 12 carbon atoms are of Type B, and only 2 of Type A. For this

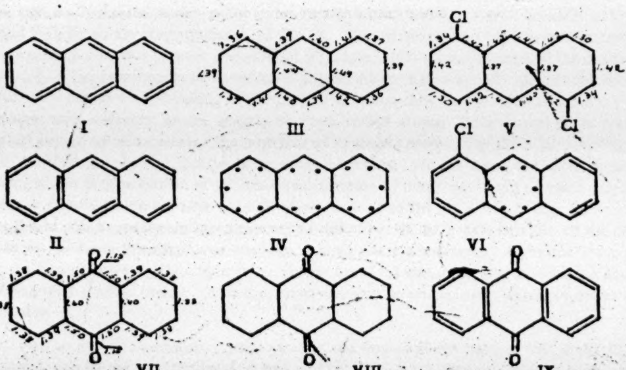
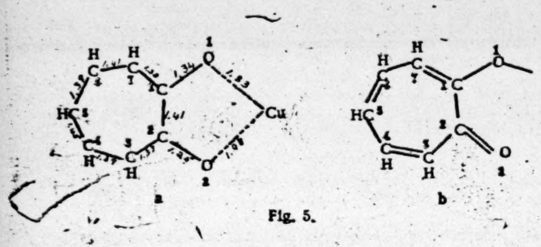


Fig. 4

molecule one might propose a Kekulé bond distribution (IX), thus making it agree with the pseudosymmetry of the molecule VII. Such a distribution of bonds, however, would be very much at variance with the interatomic distances. It follows from our discussion that there is no strictly constant localization of double bonds in the benzene rings of aromatic compounds. Under the influence of different substituents the valency electrons may be rearranged, leading to a different localization of π-bonds, or to their complete delocalization in individual benzene rings (VI–VIII) or throughout the molecule (IV).

5. As a final example let us examine the structure of tropolone (Fig. 5). Compounds of this type are characterized by being much nearer in certain properties to aromatic than to aliphatic compounds. The results of the X-ray analysis of the Cu derivative of tropolone [8] permit us to understand the nature of this phenomenon. A study of the distances between the carbon atoms shows that there is an alternation of shorter and longer bonds in six sides of the ring (see the distances between carbon atoms 1,7, 7,6, 6,5, 5,4, and 4,3), which evidently permits us to assign double character to the shorter bonds. The seventh distance, 3,2, is again short. What is the multiplicity of this bond ? The assigning of a multiplicity of two would be tantamount to the ascribing of quinquevalence to 3-C, and this, therefore, is impossible. This must therefore be a greatly shortened single bond. What is there to confirm this ? If the 3,2-bond is a single one, then the 2-oxygen is linked to 2-C by a double bond. If the bond 2-C—O is double, the bond 1-C—O is single. A comparison of the 1-C—O distance (1.34 A) with the 2-C—O distance (1.25 A) confirms such a distribution of double bonds in the molecule. The Cu—O distances also support such a distribution: 1-O has a free valency, and its distance from the copper atom is less than that of 2-O. On the other hand, the strongly electronegative oxygen (2-O) standing at a short distance from the ring of carbons attracts the hydrogen atom of the 3-CH group, thus producing a considerable shortening in the 2,3-bond and conferring benzenoid properties on the whole ring. Such is the manner in which the mutual effects of atoms are manifested in this molecule.



a b

Fig. 5.

Apart from this distribution of bonds (Fig. 5b), a second possible variant might be proposed, in favor of which may be cited the 2-C—O distance of 1.25 A, characteristic for a 1.5-fold bond, and also the exceptionally short 2,3-bond, which is shorter than any other C—C bond in the molecule. In this case we are bound to characterize the 2,3-bond as 1.5-fold, and the hydrogen, which participates in a hydrogen bond, we must consider as bound to neighboring atoms (3-C and 2-O) by single-electron bonds (C·H·O). The equivocality of the determination of the structural formula in this example does not involve a matter of principle. It is a consequence of the inadequate accuracy of the determination of the coordinates of hydrogen atoms in the crystal structure. An unequivocal answer regarding structural formulas can now be obtained in those cases in which they can be derived from the interatomic distances for atoms other than hydrogen atoms, mainly between carbon atoms. Unfortunately, the present level of X-ray analysis does not permit us to determine the positions of hydrogen atoms. For these purposes more hopeful methods are those of electronography and, particularly, neutronography. For the more restricted objects of this paper the equivocality of the determination of the structural formula of tropolone is not of great significance; what is more important is the fact that both of these possible solutions lead to the same conclusion, namely, that the "benzenoid" properties of the tropolone molecule are the result of the effect of the 2-oxygen atom on the interatomic distances. There are as yet no X-ray investigations that could supply data adequate for a consideration of the more general question of the resemblance or even identity in properties of substances having alternating double and single bonds with those having only 1.5-fold bonds; there are, however, also no obstacles in principle to the solution of these questions experimentally.

6. In conclusion we shall enumerate: 1) the assumptions that form the basis of this work; 2) the conclusions reached from an examination of the experimental material; and finally, 3) desirable further work, the performance of which could assist in the development of the ideas that have been put forward.

1) a In all compounds under examination carbon is quadrivalent, i.e., every carbon atom has 4 valency electrons. It is essential to begin with this supposition, for in a number of investigations this fact is forgotten and so not taken into account in the representation of structural formulas. Thus, according to Kitaigorodsky and Kobalkina [5], every carbon in naphthalene has on the average a valency of 4.6, and in anthracene a valency of 4.4.

b. The chemical bond between atoms in a molecule is effected by valency electrons, and a whole number of electrons participate in every bond.

c. The distance between carbon (and other) atoms, other things being equal, is the less, the greater the number of electrons participating in the formation of the bond.

2) a. The value of an interatomic distance for a given number of electrons participating in the bond may vary within fairly wide limits; thus, as a result of the mutual influence of atoms, certain bonds formed by a small number of electrons may be shorter than others formed by a greater number of electrons.

b. For the description of certain aromatic compounds having condensed benzene nuclei, the use of only single and double bonds or of only 1.5-fold (benzene) bonds is inadequate; it is necessary to consider all three types of bonds. It follows from this that every type of bond is defined by a whole number of electrons, though not necessarily an even number.

c. For every molecule it is possible to establish unequivocally the structural formula, so long as the dimensions of the molecule (the interatomic distances within it) and its symmetry have been determined with sufficient accuracy and the mutual influences of atoms have been taken into account (effect of individual atoms or groups on bond lengths).

d. Every compound is characterized by one single structure, which can be described by one single structural formula with indications of the interatomic distances. This conclusion confirms the full correctness of the Butlerov-Markovnikov theory of structure, and it reveals the invalidity of the idea of representing a molecule by two or more structural formulas.

3) a. It would be of definite interest to investigate the chemical properties of bonds equal in multiplicity but greatly differing in length and equal in length but differing in multiplicity.

b. The correlation of the structural formulas obtained with physical and chemical properties of the compounds would also be of great interest.

In order not to increase the size of the paper we have confined ourselves to these few examples; we must point out, however, that in all cases for which we were able to obtain the relevant literature the agreement of the hypotheses advanced above with the experimental data was not inferior to that found for our selected examples of aromatic compounds having condensed benzene rings. We may therefore conclude that the determination of the dimensions and symmetry of molecules is a rational method for the elucidation of the structures of organic compounds and of their representation by structural formulas and for the estimation of the mutual effects of atoms.

SUMMARY

1. It has been shown that the application of recent experimental data on interatomic distances in organic molecules makes it possible to characterize any given compound by one single structural formula.

2. It has been pointed out that the mutual effects of atoms may substantially change interatomic distances in molecules, and it is therefore necessary to take these effects into account when determining the structural formula.

3. It has been shown that for the representation of structural formulas that are compatible with the symmetry of the molecule, it is necessary in aromatic compounds having condensed benzene nuclei to take into account not only single and double bonds, but also intermediate, "1.5-fold" bonds.

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EFFECT OF THE PRESSURE APPLIED IN THE COMPRESSION OF AN ALUMINA-MOLYBDENUM OXIDE CATALYST ON ITS ACTIVITY AND STRUCTURE

O. D. Sterligov, M. G. Gonikberg, A. M. Rubinshtein, and B. A. Kazansky

In 1931 Plotnikov, Ivanov, and Pospekhov [1] showed that in the synthesis of methanol from carbon monoxide and hydrogen the activity of a ternary catalyst $Cu-ZnO-Cr_2O_3$, compressed at 300 atm was the same as that of an uncompressed catalyst of the same composition. A number of other investigators have found that at higher compression pressures there is a change in the specific activity and productivity of catalysts.* Thus, in an investigation of the decomposition reactions of methanol and ethanol on a compressed catalyst (zinc oxide) it was found [2] that increase in the compression pressure up to 5000 atm resulted in an increase in the productivity of the catalyst and a reduction in its specific activity. In more recent work [3] on the hydrogenation of mineral oils under a pressure of hydrogen in presence of compressed (up to 5000 atm) catalysts consisting of WS_2, NiS, and Al_2O_3, it was found that increase in the pressure applied in the compression of the catalysts had no significant effect on their specific activities, but somewhat increased their productivities.

Kurin and Perminov [4] made a detailed investigation of the decomposition of methanol at 275-375° in presence of a compressed zinc-chrome catalyst. According to their results, there is an appreciable rise in specific activity and productivity when the pressure at which the catalyst is compressed is increased to 5000 atm.; further increase in pressure to 10,000 atm leads to a reduction in the specific activity and productivity of the catalyst. The increase in activity of compressed catalysts was observed also by Ivannikov [5], who used a three-component catalyst $CuO-Al_2O_3-UO_3$ compressed at 20,000 atm for the esterification of ethanol in absence of acid. The activity of this catlyst was found to be greater than that of uncompressed catalyst of the same composition.

Vereshchagin, Freidlin, Rubinshtein and Numanov [6] recently showed that, in the case of the dehydration of ethanol, aluminum oxide catalyst compressed at 20,000 atm. is more effective (productive), stable, and strong than catalysts that have not been subjected to compression. Also, the authors found that the compression caused no phase change in the aluminum oxide and that structural changes in the catalyst were associated with diminution in its macroporosity.

In the cases that have been investigated, therefore, compressed catalysts were found not only to be mechanically stronger, but also to have higher productivity in comparison with uncompressed catalysts. In the majority of the investigations cited (the exceptions being [2] and [4]) no study was made of the effect of the value of the compression pressure on the catalytic properties of the catalyst. In the present work we have investigated the effect of the value of the compression pressure (over the range 2,000 - 20,000 atm.) on the structure of an alumina–molybdenum oxide catalyst and on its catalytic properties (productivity, specific activity, stability) in the reactions of dehydrocyclization of heptane and dehydrogenation of cyclohexane.

EXPERIMENTAL

Catalysts. An alumina – molybdenum oxide catalyst containing 20% by weight of MoO_3 was heated in a stream of hydrogen at 350° for 3 hours and at 500° for 2 hours. The catalyst, reduced in this way, was ground to a powder and subjected to pressure in lead ampoules under an all-direction hydrostatic pressure of 2,000 atm. Part of the compressed catalyst so obtained was then further compressed under an all-direction hydrostatic pressure of 6,000, 12,000, or 20,000 atm in lead ampoules in a superhigh-pressure multiplier. Compressed catalyst in grains 1.5-3 mm in diameter was required for the investigation. The changes, due to changes in compression pressure, in the "bulk" specific gravity of the granular catalysts obtained are given in Table 1. It follows from the data of Table 1 that the bulk specific gravity rises by 54% with increase in compression pressure from 2000 to 20,000 atm.

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* In this paper, the specific activity of a catlyst is its activity per unit weight, and its productivity is its activity per unit volume.

TABLE 1

Bulk Specific Gravity of Granular Compressed Catalysts*

Catalyst No.	Compression pressure (atm)	Bulk specific gravity (g/cm³)
1	2000	0.78
2	6000	0.79
3	12000	1.00
4	20000	1.20

Apparatus, Procedure, and Method of Investigating Catalysts. The experiments were carried out without the use of a gas-carrier, the flow method being employed. The pressure was atmospheric in the catalysis tube (length 1100 mm, internal diameter 7 mm), which was made of Pyrex glass and was mounted on an inclined catalysis furnace provided with electric heating and temperature regulation. In all experiments on the determination of the activity of the catalysts, the temperature was maintained in the range 489-491°. A layer of catalyst 16.5 cm long was placed in the catalysis tube. All experiments were carried out with 6cm³ of catalyst (always measured in the same glass cylinder). In the main experiments the duration was 4 hours, but in those on productivity it was 2-4 hours. In the experiments, regenerated catalysts of stable activity were always used. In order to stabilize their activities, fresh portions of catalyst were heated in a stream of hydrogen for 2 hours at 500°, after which a 2-hour experiment with heptane at 489-491° was carried out. The catalyst was then regenerated (this was done also after other experiments under the same conditions): the catalyst was blown with nitrogen for 30 minutes, then with air at 500° for about one hour, after which air was displaced by nitrogen and the catalyst was reduced with hydrogen at 500° for 1-2 hours. When these operating conditions were observed with the catalyst, the experiments were found to be sufficiently reproducible.

Hydrocarbons having the following constants were used: heptane — b.p. 98.2 - 98.3° at 760 mm; d_4^{20} 0.6838; n_D^{20} 1.3876 (literature [8] gives: b.p. 98.4° at 760 mm; d_4^{20} 0.6837, n_D^{20} 1.3876); cyclohexane — b.p. 80.7°- 80.8° at 760 mm; d_4^{20} 0.7785; n_D^{20} 1.4265 (literature [8] gives: b.p. 80.7° at 760 mm; d_4^{20} 0.7786; n_D^{20} 1.4262).

During the experiments the hydrocarbons were passed to the catalysis tube always at the same space velocity of 0.59 ml of hydrocarbon per 1cm³ of catalyst per hour; this was carried out with the aid of a piston device for delivering liquids at a constant rate [7]. The device was operated by means of a small CD-2 motor. The catalyzate passed from the reaction tube to a receiver cooled by a mixture of ice and water and connected to a trap cooled to −70°. In order to remove the small amount of catalyzate that was generally held back at the end of the catalysis tube, the latter was provided with a special drain made from aluminum foil. The weight of the liquid that collected in the trap during the experiment was divided by the number of hours that had passed, and the result was added to the weight of catalyzate obtained per hour in the given experiment. At the end of each experiment, starting substances adsorbed by the catalyst and reaction products were displaced by nitrogen and their weight determined so that it might be added to the weight of catalyzate obtained in the first hour of the experiment.

In the course of the experiments catalyzates were collected separately every hour, and their refractive indices and yields (g) were determined. At the end of the experiment all the

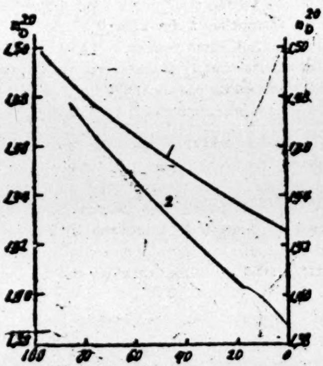

Fig. 1. Dependence of the refractive index n_D^{20} of catalyzate on its content of aromatic hydrocarbons: 1) Cyclohexane catalyzates; 2) heptane catalyzates (x is the concentration of aromatic hydrocarbons in the catalyzate in % by weight).

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* The bulk specific gravity was determined by weighing 6 cc of catalyst (in grains of diameter 1.5-3mm) measured in a particular glass cylinder having a capacity of 10 ml.

catalyzates collected were united, and the refractive index of the catalyzate obtained over the whole course of the experiment was determined. For the determination of the degree of conversion of heptane or cyclohexane into aromatic hydrocarbons, we made use of curves relating the refractive indices of the catalyzates from these hydrocarbons to their contents of aromatic hydrocarbons. The relevant curves, which are given in Fig. 1, were constructed on the basis of investigations of 60 catalyzates from heptane and 54 catalyzates from cyclohexane, which were obtained in the presence of alumina–molybdenum oxide catalysts at 450-500°, the concentration of aromatic hydrocarbons being determined by the method of relative dispersions proposed by Ioffe [9, 10]. The curves given cover data on the refractive indices of catalysts containing from 6 to 97% of aromatic hydrocarbons.

TABLE 2

Activity of Compressed Catalysts in the Dehydrocyclization of Heptane*

Expt. No.	Catalyst No.	Compression pressure (atm)	Time (hr)	Amt. of hydrocarbons passed (ml)	Yield of catalyzate (% by wt.)	n_D^{20} of catalyzate	Content of aromatic hydrocarbons in catalyzate (% by wt)	Productivity of catalyzate	Specific activity of catalyzate
126	1	2000	0-1	3.50	67.8	1.4182	33.9	3.83	4.91
			1-2	3.50	79.9	1.4076	22.3	2.97	3.81
			2-3	3.55	86.9	1.4028	16.5	2.45	3.13
			3-4	3.55	88.5	1.4001	12.1	1.78	2.29
		Total		14.10					
		Mean			81.3	1.4057	20.5	2.78	3.56
121	2	6000	0-1	3.55	58.0	1.4214	37.0	3.58	4.56
			1-2	3.60	83.3	1.4082	23.1	3.20	4.08
			2-3	3.50	85.8	1.4035	17.5	2.50	3.19
			3-4	3.60	88.2	1.4003	12.8	1.88	2.40
		Total		14.25					
		Mean			78.9	1.4063	21.0	2.77	3.52
116	3	1200	0-1	3.50	64.4	1.4236	39.0	4.22	4.17
			1-2	3.60	85.4	1.4080	22.5	3.20	3.19
			2-3	3.50	85.4	1.4026	16.5	2.35	2.35
			3-4	3.60	87.0	1.4008	13.7	1.98	1.98
		Total		14.20					
		Mean			80.6	1.4070	21.8	2.93	2.93
132	4	20000	0-1	3.50	60.7	1.4245	39.9	4.04	3.36
			1-2	3.60	75.6	1.4134	28.5	3.58	2.98
			2-3	3.50	88.3	1.4066	21.1	3.10	2.58
			3-4	3.55	86.4	1.4028	16.8	2.42	2.01
		Total		14.15					
		Mean			77.8	1.4093	24.1	3.13	2.61

Results of the Investigation of the Activity of Compressed Catalysts. As indicated above, the object of this work was the elucidation of the effect of the value of the pressure applied in the compression of catalysts on their catalytic properties. In Tables 2 and 3 results are given that characterize the effect of the pressure applied in the compression of catalysts on their activity in the reactions of dehydrocyclization of heptane and dehydrogenation of cyclohexane. We determined the activity in the form of the degree of conversion (in % by wt.) of the original hydrocarbons into aromatics referred to 1cm^3 of catalyst (productivity) or to 1 g of catalyst (specific activity) at constant space rate (0.59 ml of hydrocarbon per 1cm^3 of catalyst per hour).

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* Space rate 0.59; temperature of experiments 489-491°; volume of catalyst 6 cm^3.

TABLE 3

Activity of Compressed Catalysts in the Dehydrogenation of Cyclohexane *

Expt. No.	Catalyst No.	Compression pressure (atm)	Time (hr)	Amt. of hydrocarbons passed (ml)	Yield of catalyzate (% by wt.)	n_D^{20} of catalyzate	Content of aromatic hydrocarbons in catalyzate (% by wt.)	Productivity of catalyzate	Specific activity of catalyzate
128	1	2000	0-1 1-2 2-3 3-4	3.60 3.50 3.50 3.55	71.4 82.7 88.6 89.1	1.4683 1.4566 1.4513 1.4464	65.0 49.8 41.9 34.2	7.73 6.86 6.18 5.08	9.92 8.80 7.93 6.51
		Total		14.15					
		Mean			82.9	1.4541	46.0	6.35	8.15
124	2	6000	0-1 1-2 2-3 3-4	3.50 3.50 3.55 3.50	72.1 85.3 89.5 90.8	1.4671 1.4564 1.4497 1.4454	63.9 49.5 39.8 32.9	7.68 7.03 5.93 4.98	9.78 8.96 7.56 6.34
		Total		14.05					
		Mean			84.4	1.4526	43.9	6.18	7.88
119	3	12000	0-1 1-2 2-3 3-4	3.60 3.50 3.55 3.50	67.1 83.5 87.0 86.4	1.4717 1.4624 1.4558 1.4517	69.0 57.4 48.3 42.2	7.71 7.98 7.00 6.08	7.70 7.97 6.99 6.07
		Total		14.15					
		Mean			80.9	1.4587	52.5	7.09	7.07
136	4	20000	0-1 1-2 2-3 3-4	3.50 3.50 3.60 3.50	78.3 84.2 85.7 88.2	1.4703 1.4578 1.4561 1.4533	67.8 51.0 48.9 44.5	8.86 7.15 6.99 6.53	7.36 5.96 5.81 5.44
		Total		14.10					
		Mean			84.1	1.4582	51.7	7.25	6.03

Examination of the results in Tables 2 and 3 permits us to conclude that increase in the pressure applied in the compression of an alumina–molybdenum oxide catalyst leads to a rise in its productivity. At the same time, the results indicate a reduction in the specific activity of compressed catalysts, in the reactions we have investigated, as the pressure applied for their compression is increased.

Results of X-ray Investigations of Catalysts. Investigations were carried out on samples of catalysts that had been reduced but not yet used for the aromatization of the hydrocarbons. Photographs were taken on Kodak film in a Debye camera, having a film holder 57 mm in diameter, by means of the series K_α rays of iron (λ = 1.932A), the exposure being 10 hours at 12 mA and 30 kV.

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* Space rate 0.59; temperature of experiments 489-491°; volume of catalyst 6 cm^3.

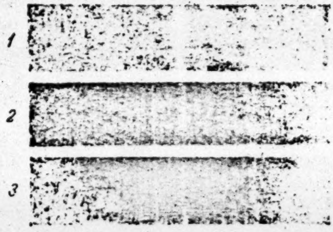

Fig. 2. X-Ray diffraction photographs.

1) Uncompressed catalyst;

2) Catalyst No. 1.

3) Catalyst No. 3.

The X-ray photographs of the original catalyst and of samples compressed at pressures of 2000 and 12,000 atm are given in Fig. 2 (see page 29). The identical positions of the lines and the identical widths of corresponding lines on all of the X-ray photographs indicate that, firstly, compression at pressures of up to 12,000 atm does not result in any change in the phase composition of the mixed catalyst under investigation, and, secondly, the dimensions of the elementary crystals (i.e., the degree of dispersion) are not affected over this range of pressures.

TABLE 4

Results of the X-Ray Analysis of Alumina—Molybdenum Oxide Catalysts

Uncompressed sample		Catalyst No. 1 (compressed at 2,000 atm)		Catalyst No. 3 (compressed at 12,000 atm)	
d (A)	Intensity	d (A)	Intensity	d (A)	Intensity
2.24	medium	2.24	medium	2.24	medium
2.09	v. weak	2.05	v. weak	2.07	v. weak
1.88	strong	1.87	strong	1.89	strong
1.63	v. weak	—	—	1.65	v. weak
1.47	medium	1.47	medium	—	—
1.35	v. strong	1.34	v. strong	1.36	v. strong
1.17	weak	—	—	—	—
1.13	weak	1.12	weak	1.12	weak

The X-ray results in Table 4 show that the values of the interplanar distances (d) for catalysts Nos. 1 and 3 have changed to such an insignificant extent from those for the uncompressed catalyst that the observed variations could be assigned entirely to experimental error. Exceptions are found in the values of d for the very weak lines, the exact measurement of which is difficult. The results in Table 4 show also that the crystalline phase in the investigated samples is γ-Al_2O_3, having a somewhat deformed lattice, evidently owing to the dissolution in it of part of the MoO_2 present in the catalyst. As the catalysts have the characteristic color of MoO_2, it must be considered that an appreciable part of it is present as an independent phase, in spite of the absence of MoO_2 lines in the X-ray photographs. This view is confirmed by results for the values of the parameter of the crystal lattice of γ-Al_2O_3 and the deformation of the lattice; these are given in Table 5.

TABLE 5

Deformation of the Crystal Lattice of γ-Al_2O_3 in the Samples Investigated

Sample	a (A)	Deformation relative to uncompressed sample (%)	Deformation relative to value of a from tables	
			(%)	(A)
Uncompressed	7.75	—	−2.0	0.16
Catalyst No. 1 (compressed at 2000 atm)	7.72	−0.37	−2.4	0.19
Catalyst No. 3 (compressed at 12,000 atm)	7.74	−0.14	−2.2	0.17
Value from tables	7.91			

Thus, already in its original condition the catalyst contains γ-Al_2O_3 having a deformed lattice, its mean compression amounting to 0.18 A or 2.2%. In view of the values of the parameters of the lattice of MoO_2 (c = 4.86A, a = 2.88A, rutile type), the observed change in the parameter of the lattice of γ-Al_2O_3 indicates the formation of a solid solution containing a low concentration of MoO_2. As the MoO_2 content of the catalyst is considerable (about 20%) and there are no corresponding reflections on the X-ray photographs, it must be concluded that the part of the MoO_2 that has not passed into the lattice of γ-Al_2O_3 is in a state that is amorphous to X-rays. The practically constant value of the lattice deformation of γ-Al_2O_3 at various pressures indicates that the compression did not affect the composition of the solid solution.

The general conclusion from the X-ray analysis of the samples of catalyst is as follows: compression at pressures of up to 12,000 atm does not cause any change in the phase composition and primary (X-ray) structure of the investigated catalyst. The observed changes in its physical properties (increase in bulk specific gravity, hardness, and strength) must be attributed to changes in secondary structure, in particular, porosity.

DISCUSSION OF RESULTS

The results obtained in this investigation have extended our information on the effect of the pressure applied in the compression of catalysts on their activity. These results lead to the conclusion that the productivity of the compressed catalysts that we have investigated is determined by two quantities: the specific activity and the bulk specific gravity, which change in opposite directions as the compression pressure is increased.

It follows from an examination of Fig. 3, that increase in the compression pressure from 2000 to 20,000 atm leads to an increase in the productivity of the catalyst in both of the investigated reactions by 12-14%; under these conditions the specific activity falls by 26-27%. The absence of significant changes in the crystalline structure of the catalysts after their subjection to a hydrostatic pressure is evidence for the supposition that the observed fall in specific activity is associated with the change in the porosity of the catalyst.

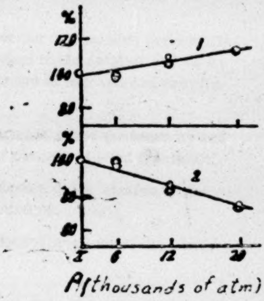

Fig. 3. Effect of compression pressure on productivity (1) and specific activity (2) of alumina-molybdenum oxide catalysts: o – dehydrocyclization of heptane; • – dehydrogenation of cyclohexane.

Let us pass to an examination of the stability of compressed catalyst. Analysis of the results given in Tables 2 and 3 shows that reduction in the specific activity of the catalyst (c) with increase in the duration of the experiment τ may be expressed by a straight line on the graph of log c against τ (Fig. 4), i.e. by the equation:

$$\log c = \log c_0 - \alpha\tau.$$

In this equation c_0 is the specific activity of the catalyst at $\tau = 0$; the value of the coefficient α characterizes the rate at which the specific activity of the catalyst falls in the course of use (instability of the catalyst). It is found desirable to characterize the stability of the catalyst by the coefficient β, equal to $1/\alpha$. The value of the stability coefficient β increases with increase in the compression pressure (Table 6). We have as yet no basis, however, upon which to conclude that this increase in stability is a specific effect of the high compression pressure. We cannot exclude the possibility that the observed increase in the stability of compressed catalysts is associated with their reduced specific activity, as has been observed in a number of cases for uncompressed catalysts. In order to solve this important question, further investigations are required.

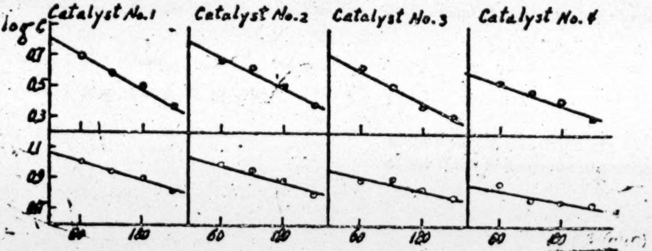

Fig. 4. Stability of compressed alumina-molybdenum oxide catalysts in [illegible] of use: o – dehydrocyclization of heptane; • – dehydrogenation of cyclohexane (c is the specific activity of the catalyst).

In conclusion we may point out that the increase in the coefficient β is approximately the same for both of the investigated reactions (67-77 %).

TABLE 6

Effect of the Pressure Applied in the Compression of Catalysts on the Value of the Stability Coefficient β.

Pressure p (atm)	Dehydrogenation of cyclohexane		Dehydrocyclization of heptane	
	β (hr)	$\beta_p : \beta_{2000}$	β (hr)	$\beta_p : \beta_{2000}$
2000	17.4	1.00	8.9	1.00
6000	18.2	1.05	10.2	1.15
12000	22.2	1.28	10.0	1.12
20000	30.7	1.77	14.8	1.67

SUMMARY

1. An investigation has been carried out into the effect of the value of the compression pressure (in the range 2000-20,000 atm) on the structure of compressed alumina—molybdenum oxide catalyst and on its productivity, specific activity, and stability in the reactions of dehydrocyclization of heptane and dehydrogenation of cyclohexane.

2. It has been shown that increase in compression pressure leads to increase in the productivity and decrease in the specific activity of the catalyst (to an equal extent for both of the investigated reactions).

3. It has been found that the stability of compressed alumina—molybdenum oxide catalyst increases with the compression pressure (also to an equal extent for both of the investigated reactions).

4. X-Ray investigation has not revealed any changes in the primary (X-ray) structure of the catalyst after it has been subjected to a high hydrostatic pressure.

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ADSORPTION OF GAS MIXTURES

COMMUNICATION 3. POSSIBILITY OF A STATISTICAL TREATMENT OF THE ADSORPTION PHENOMENA OF GAS MIXTURES

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We shall consider that the fundamental problem in the theory of the adsorption of gas mixtures is the calculation of the adsorption of the components of the mixture for given values of the equilibrium partial pressures, the isotherms for the adsorption of the pure components being known at the same temperature. If we confine ourselves to the examination of the binary mixtures, this problem may be formulated as follows: it is required to calculate the values of the functions

$$a_1 = f_1(p_1, p_2) \quad \text{and} \quad a_2 = f_2(p_1, p_2) \tag{1}$$

the functions $a_1^* = f_1(p_1, 0)$ and $a_2^* = f_2(0, p_2)$ being given (graphically or analytically); a_1 and a_2 are the adsorption values for the components of the mixture; a_1^* and a_2^* are the corresponding values for the adsorption of pure component; and p_1 and p_2 are the equilibrium partial pressures (here and elsewhere in this paper the gas phase is considered to be ideal).

In the solution of this problem we may start from different physical representations of the adsorption process. It may be assumed, of course, that any molecular—kinetic or thermodynamic theory of adsorption may be generalized to the case of the adsorption of a mixture. This generalization may sometimes be performed without the introduction of any new constants, i.e., all the constants necessary for the description of the adsorption of a mixture may be obtained by the investigation of the adsorption of the pure components. It is obvious that in this case the solution of the problem stated above is possible. Such a case is found in the well-known simple theory of Langmuir adsorption. In certain cases a similar generalization is in principle impossible without the introduction of some new constants. Magnus' theory [1] is one of this type. It will be clear that in these cases the functions $a_1^* = f_1(p_1, 0)$ and $a_2^* = f_2(0, p_2)$ are insufficient for the calculation of the functions expressed by Equations 1.

In this paper we shall confine ourselves to the examination of certain aspects of the theory of adsorption of binary gas mixtures, the postulate being made that in the system under investigation all prerequisites demanded by Langmuir's theory are realized with the exception of the assumption of energetic homogeneity over the surface. As is well known, Langmuir himself pointed out that for surfaces having adsorption sites of several types it is possible to apply the concepts relating to a homogeneous surface to each assembly of identical sites and to calculated the adsorption over the whole surface by summation of the adsorption values for all the assemblies. This demonstration, however, remained in the form of a schematic formula, for there were no methods available for the practical performance of such a calculation. Substantial progress in this direction was made by Zeldovich [2], who, in the place of a discreet set of energies of adsorption, introduced a continuous function for the surface distribution according to adsorption energy values (or adsorption coefficient values) and found an analytical expression for the adsorption isotherm for a definite form of this distribution function. This line of work, mainly as a result of Roginsky's investigations, developed into an orderly theory of adsorption and catalytic phenomena on heterogeneous surfaces. A detailed exposition of the theory and its numerous applications, and also a history of the question, are given by Roginsky in his monograph [3].

It must be pointed out that Roginsky and Todes [4] have extended this theory to the case of the adsorption of gas mixtures and, with the aid of certain supplementary assumptions, have solved the problem formulated at the beginning of this paper. In a later part of this paper we shall compare the results obtained by Roginsky and Todes with the results of the analysis of the problem that now follows.

Let us assume that the surface may be characterized by a distribution function $\rho(b_1, b_2)$ in terms of two adsorption coefficients b_1 and b_2, which may in general be regarded as independent variables. It is evident that

$$\int_0^\infty\int_0^\infty \rho(b_1, b_2)\, db_1\, db_2 = 1 \tag{2}$$

In the case of adsorption from a mixture, the degree of filling of the surface by, for example, the first component will be expressed in its most general form, with all the assumptions already made, by the following equation:

$$\theta_1 = \int_0^\infty\int_0^\infty \frac{b_1 p_1}{1 + \sum_1 b_i p_i} \rho(b_1, b_2)\, db_1 db_2. \tag{3}$$

From the very beginning we shall confine ourselves to a consideration of the case in which b_2 is a single-valued function of b_1. On the basis of very general considerations, it may be concluded that this case is always realized in physical adsorption. If $b_2 = \varphi(b_1)$, then $\rho(b_1, b_2) = \rho[b_1, \varphi(b_1)] = \rho(b_1)$, and for the calculation of the degree of filling a knowledge of the distribution functions, e.g., with respect to b_1, is sufficient. Equation 3 may be simplified and written as follows:

$$\theta_1 = \int_0^\infty \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1; \qquad \theta_2 = \int_0^\infty \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1; \tag{4a}$$

$$\theta_{12} = \theta_1 + \theta_2 = \int_0^\infty \frac{b_1 p_1 + b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1. \tag{4b}$$

It may be noted that for the sake of generality integration limits of zero and infinity have been indicated in Equations 4; it is in fact sufficient to integrate from a certain $b_{1\,min}$ to a certain $b_{1\,max}$, since for values of b_1 higher than $b_{1\,max}$ and less than $b_{1\,min}$, the function $\rho(b_1)$ becomes zero.

There is reason to suppose that in the most general case no further simplifications of Equations 4 are possible. The possibility of utilizing these equations practically is now determined by the possibility of the reliable determination of the function $\rho(b_1)$, from investigation of the adsorption of the pure component, and of the function $b_2 = \varphi(b_1)$, from some other considerations. Considerable interest is presented, however, by the examination of various special cases in which certain assumptions concerning the form of the functions $b_2 = \varphi(b_1)$ or $\rho(b_1)$ permit us to proceed very much further instead of confining ourselves to the simple writing out of Equations 4.

It may be noted further that for the complete description of the adsorption equilibrium in the case of a gas mixture, it is possible to calculate, instead of the quantities a_1 and a_2 (or θ_1 and θ_2), the values of the total adsorption $a_{12} = a_1 + a_2$ (or $\theta_{12} = \theta_1 + \theta_2$) and of the so-called selectivity coefficient α_2 [5], defined by the equation:

$$\alpha_2 = \frac{N_2^\sigma N_1}{N_1^\sigma N_2} = \frac{a_2 p_1}{a_1 p_2} = \frac{\theta_2 p_1}{\theta_1 p_2} \tag{5}$$

(here N_2^σ and $N_1^\sigma = 1 - N_2^\sigma$ are the molar fractions of the components in the adsorbed phase, and N_2 and $N_1 = 1 - N_2$ are the corresponding quantities for the equilibrium gas phase). It is clear that a knowledge of the values of a_{12} and α_2 for given values of the independent variables p_1 and p_2 will permit us to calculate the corresponding values of a_1 and a_2.

The first case that we shall examine is a completely trivial one. For a homogeneous surface (as a special case of a heterogeneous one), Equations 4 may be clearly written in the form:

$$\theta_1 = \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2}; \quad \theta_2 = \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2}; \tag{6a}$$

$$\theta_{12} = \frac{b_1 p_1 + b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \tag{6b}$$

It must be emphasized that in the expression $\theta_i = \frac{a_i}{a^m}$ where a^m is the maximum adsorption in a monomolecular layer, the value of a^m is the same for each component. The alternative supposition is not compatible with the molecular-kinetic picture upon which the concept that we are discussing is based, and it leads to a thermodynamic contradiction. We have examined this question in detail [5]. •

• After the publication of our paper [5] we learned of a paper which had previously escaped notice, by I. R. Krichevsky, (J. Phys. Chem., 5, 742, 1934), in which, long before our work and with exhaustive completeness and rigor, the incompatability of the postulate $a_1^m \neq a_2^{mc}$ with the Gibbs-Duhem equation was proved.

From this point of view the well known work of Markham and Benton [6] on the adsorption of gas mixtures is not valid, since it is there assumed that $a_1^m \neq a_2^m$. For the same reason certain conclusions of Lewis and coworkers [7] are invalid: they also assume that $a_1^m \neq a_2^m$.

Since the coefficients b_1 and b_2 can readily be determined for a homogeneous surface from data on the absorption of the pure components, Equations 6 give a complete solution to this problem.

For our further considerations, the following remarks are of importance. If we plot equilibrium partial pressures p_1 and p_2 along two axes of coordinates (Fig. 1) and values of a_1, a_2, or a_{12} along the third axis, then it follows from Equations 6 that the projections of the summation isosteres of adsorption a_{12} = const. on the plane $a_1 = 0$ form a family of parallel straight lines having slopes of $-b_1/b_2$; the projections of the adsorption isosteres of the first component of the mixture on the same plane form a family of straight lines, which, when continued, intersect at one point having the coordinates $(0, -1/b_2)$; the rectilinear isosteres for the second component, when continued, also intersect at one point, which has the coordinates $(-1/b_1, 0)$.

From Equations 6 it follows that the selectivity coefficient in the case of a homogeneous surface does not depend on p_1 and p_2 and is equal to the ratio of the coefficients b_2 and b_1:

$$\alpha_2 = \frac{b_2}{b_1}. \tag{7}$$

The second special case that we shall examine concerns a heterogeneous surface, and it may be formulated as follows. Let the difference in the energy of adsorption for a transition from adsorption sites of one type to those of another be the same for each component:

$$\epsilon_2 - \epsilon_1 = \text{const.} \tag{8}$$

Since

$$b_1 = b_{10} e^{\epsilon_1/RT} \tag{9}$$

(b_{10} — is a certain constant, the physical significance of which we shall consider later), the condition of Equation 8 is equivalent to the condition:

$$\frac{b_2}{b_1} = \frac{b_{20}}{b_{10}} e^{(\epsilon_2 - \epsilon_1)/RT} = k = \text{const.} \tag{10}$$

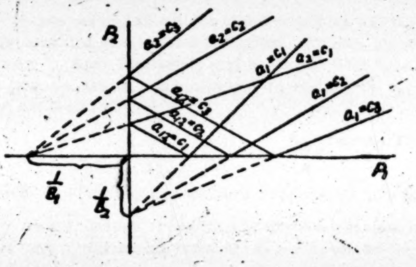

Figure 1.

By the use of Equation 10 and an examination of the total adsorption isotherm (a_{12} = const.), we may rewrite Equation 4b in the form:

$$\theta_{12} = \frac{a_{12}}{a^m} = \int_0^\infty \frac{p_1 + kp_2}{\frac{1}{b_1} + p_1 + kp_2} \rho(b_1) db_1 = \text{const.} \tag{11}$$

Equation 11 enables us to determine the form of the curve $p_2 = \varphi(p_1)$, along which a_{12} remains constant (in other words, enables us to determine the equation of the projection of the isostere for total adsorption on the plane $a_1 = 0$). It is clear that along this curve

$$\frac{1}{a^m} \frac{da_{12}}{dp_1} = \int_0^\infty \frac{\frac{1}{b_1}\left(1 + k\frac{dp_2}{dp_1}\right)}{\left(\frac{1}{b_1} + p_1 + kp_2\right)^2} \rho(b_1) db_1 = 0. \tag{12}$$

Equation 12 is satisfied if

$$1 + k\frac{dp_2}{dp_1} = 0 . \qquad (13)$$

Equation 12 has no other solutions, for in accordance with the physical sense of the quantities involved in it, the function

$$\frac{\frac{1}{b_1}\rho(b_1)}{\left(\frac{1}{b_1} + p_1 + kp_2\right)^2}$$

is essentially positive.

It follows from Equation 13 that

$$p_2 = -\frac{1}{k}p_1 + C . \qquad (14)$$

When the condition of Equation 8 is observed, therefore, irrespective of the form of the distribution function, the projections of the total adsorption isosteres on the plane $a_1 = 0$ are straight lines.*

In the second communication [8] of this series it was shown that, in all of the cases that we have examined of the adsorption of binary mixtures of gases, the projections of the total adsorption isosteres on the plane $a_1 = 0$ are indeed straight lines. It is, however, difficult, if not impossible, to imagine an adsorption mechanism for which the condition of Equation 8 would be realized. The question of the conditions under which Equation 14 can be fulfilled (exactly or approximately), apart from the case defined by Equation 8, is therefore of some interest.

Before making an analysis of this matter we will show how the selectivity coefficient α can be expressed when the condition of Equation 8 is observed. For each given type of adsorption sites the coefficient α is expressed by Equation 7. Since Equation 10 may be derived from Equation 8, in this case α remains constant for the whole surface (with the natural assumption that the coefficients b_{i0} do not change on passing from one type of sites to another) and is given by

$$\alpha_2 = \frac{b_{20}}{b_{10}}e^{(\epsilon_2 - \epsilon_1)/RT} . \qquad (15)$$

The possibility of making an approximate calculation from Equation 15 will be discussed below.

An examination of possible adsorption mechanisms leads to the view that for physical adsorption the most probable form of relationship between ϵ_2 and ϵ_1 will be

$$\frac{\epsilon_2}{\epsilon_1} = \beta \qquad (16)$$

where β is some constant, which, in the case of adsorption due to dispersion forces, for example, is equal to the first approximation to the ratio of the polarizabilities of the molecules of the two components. From Equations 16 and 9 we may write

$$\frac{b_2}{b_1} = \frac{b_{20}}{b_{10}^{\beta}}\, b_1^{\beta-1} = k'b_1^{\beta-1} , \qquad (17)$$

where k' is a constant. Comparison of Equations 10 and 17 shows that when β is sufficiently close in value to unity (i.e. in the case when the adsorption energies of the two components are very close together in value) all the conclusions that can be rigorously drawn from Equation 10 are approximately true also when the condition in Equation 16 is observed, the closeness of the approximation being the greater, the lower the value of $\delta = \beta - 1$.

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* In a discussion of the questions examined in this paper, S. Z. Roginsky pointed out to us that Equation 14 could be obtained from a comparison of the equation

$$\theta_1' = \int_0^{\infty} \frac{b_1 p_1}{1 + b_1 p_1}\, \rho(b_1) db_1$$

with Equation 4b, the additional postulate that $\theta_1' = \theta_{12}'$ being made.

Thus, when the condition most frequently realized in practice, i.e. that expressed in Equation 16, is observed, and at sufficiently low values of δ, irrespective of the form of the distribution function, Equations 14 and 15 must be approximately correct. In the limit, when $\delta = 0$, the condition of Equation 16 becomes equivalent to that of Equation 8, and Equations 14 and 15 become strictly accurate.

It is easy to show that the second limiting case, when the components of the mixture differ greatly in their adsorption energies (more exactly, when $\epsilon_2 - \epsilon_1 \gg RT$, which is practically equivalent to the condition that β must be a quantity of the order of unity or greater), corresponds to the solution given by Roginsky and Todes [4] (with the supplementary condition that $\epsilon_{1\,max} - \epsilon_{1\,min} \gg 4RT$). As these authors do not make sufficiently clear that their solution is valid only under the condition that $\epsilon_2 - \epsilon_1 \gg RT$ [*], we considered it desirable to discuss this matter briefly. We shall confine ourselves to an analysis of only two of the conclusions that Roginsky and Todes reach.

The ratio of the degrees of filling of a given type of adsorption site by the two components is calculated by Roginsky and Todes from a formula that has the following form in our notation:

$$\frac{\theta_2}{\theta_1} = \frac{b_{20}}{b_{10}} \frac{p_1}{p_2} e^{\epsilon_1(\beta-1)/RT}. \tag{18}$$

If p_1 and p_2 are of the same order (and all the more if $p_2 \gg p_1$), Roginsky and Todes consider that for all types of sites the value of θ_1 may be neglected in comparison with θ_2. It is clear that this conclusion is valid only if $\epsilon_1(\beta-1) \gg RT$. For sufficiently high values of p_2, θ_2/θ_1 may attain the value of unity (for a definite value of $\epsilon_1 = \epsilon_1^*$) From Equation 18 we obtain

$$\epsilon_1^* = \frac{RT}{\beta - 1} \ln \frac{p_2 b_{10}}{p_1 b_{20}}. \tag{19}$$

Roginsky and Todes consider that when $\epsilon_1 > \epsilon_1^*$, then θ_1 may be neglected in comparison with θ_2, and when $\epsilon_1 < \epsilon_1^*$, then θ_2 may be neglected in comparison with θ_1. It is quite obvious that this conclusion is valid only when $\epsilon_1(\beta - 1) \gg RT$, and this condition is practically equivalent to the condition $\beta \gg 1$.

It should be pointed out that among the cases considered by Roginsky and Todes there is one for which the condition $\beta \gg 1$ is not required. This is the case when there is no correlation between the adsorption energies of the separate components. It was for this case, however, that these authors did not find it possible to exclude the distribution coefficient from the expressions for the adsorption of the mixture.

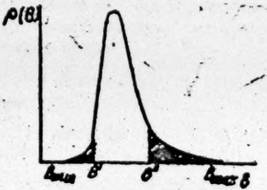

Fig. 2.

Let us return again to the analysis of Equations 4. It may be considered that in the investigation of physical adsorption the most interesting case from the practical point of view occurs when the condition in Equation 16 is observed and the value of β, although close to unity, is not so close that Equation 10 may be considered a good approximation to Equation 17. In this case, a fairly good approximate solution of the problem is possible if a certain limitation (in our opinion, a quite natural limitation) is placed on the form of the distribution function. We shall consider that the distribution function has a fairly sharp maximum. Physically, this means that, although types of sites associated with widely differing adsorption energies (and therefore adsorption coefficients) are to be found on the surface, the proportion of such sites is comparatively low. In other words, the integration in Equations 4 may be carried out, to a good approximation, by using as limits not b_{min} and b_{max}, but the considerably narrower limits b' and b'' (Fig. 2), b' and b'' being such that outside them the distribution function has values not far removed from zero. It is clear that this method of integration implies the neglecting of the area shaded in Fig. 2 in comparison with the whole area under the curve. It is obvious that the positions of b' and b'' cannot be fixed exactly; they are determined by the form of the distribution curve and the desired degree of accuracy. It is clear also that such a method of integration is inapplicable for very low degrees of filling, for which the rejected types of sites may play a decisive part.

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[*] The condition $\epsilon_{1\,max} - \epsilon_{1\,min} \gg 4RT$ is expressed quite clearly by these authors.

Let us determine by what factor the ratio b_2/b_1 may change in the chosen range from b' to b''. From Equations 17 and 9 we may write

$$\frac{b_2''}{b_1''} : \frac{b_2'}{b_1'} = e^{(\epsilon_1''-\epsilon_1')(\beta-1)/RT} \qquad (20)$$

where ϵ_1'' and ϵ_1' are values of the adsorption energy of the first component corresponding to sites having adsorption coefficients b_1'' and b_1'.

Equation 20 shows that, in the case under examination, b_2/b_1 may be the better approximated by means of some constant (within the range b_2''/b_1'' to b_2'/b_1'), the lower the value of $(\epsilon_1''-\epsilon_1')(\beta-1)$ in comparison with RT. Again, for a given degree of accuracy in such an approximation, the less the difference in the adsorption energies of the two components, i.e. the nearer β is to unity, the less is the need for narrowness in the interval $\epsilon_1''-\epsilon_1'$. In the limit, when $\beta = 1$, this interval may be as wide as we like. On the other hand, the narrower the interval $\epsilon_1''-\epsilon_1'$, the less the limitations to the value of β. In the limit, when $\epsilon_1''-\epsilon_1'$ is very small, β may have any value we like. In the general case, as already stated, the possibility of approximating b_2/b_1 by means of some constant is determined by two factors: an insignificant difference in energies of adsorption and a comparatively narrow "range of heterogeneity" over the main part of the surface. It was shown above that, if $b_2/b_1 \approx$ const, then Equations 14 and 15 are approximately true.

We consider that the case characterized by the condition:

$$(\epsilon_1''-\epsilon_1')(\beta-1) \ll RT \qquad (21)$$

unlike the limiting cases already examined, is fairly frequently realized in practice.

This assertion, of course, cannot be proved directly, for we do not know the values of the local adsorption energies ϵ; in its support, however, we can advance a number of indirect arguments. Comparison of experimentally determined heats of adsorption for various gases on the same adsorbent and attempts to evaluate the relative local adsorption energies of different gases on a definite type of adsorption sites from the relative polarizabilities of these molecules show that the factor $(\beta-1)$ very often has the value 0.1 - 0.3. With regard to the factor $(\epsilon_1''-\epsilon_1')$, although its quantitative evaluation does not appear to be possible, there is reason to suppose that it is small for the adsorbents that are most important practically (active carbons, silica gels). For silica gels this conclusion follows from the experiments, for example, of Kiselev and coworkers [9], who showed that there was practically complete coincidence between the so-called "absolute" adsorption isotherms of nitrogen and other vapors on silica gels of differing origins and structures. As it is improbable that such different silica gels would have surfaces of identical heterogeneity, it must be considered that a substantial part of their surfaces is fairly homogeneous, which means, of course, that the difference $(\epsilon_1''-\epsilon_1')$ is small.

For active carbons, the following considerations are presented as indirect confirmation of this point of view:

1. Adsorption isotherms for carbons can often be well described by interpolation formulas of the type $a = kp^{1/n}$; as is well known, the statistical theory of adsorption [2,3] leads in this case to an exponential distribution of the surface with respect to the values of local adsorption energies, i.e. to narrowness of the interval $\epsilon_1''-\epsilon_1'$.

2. With increase in the degree of filling of the surface, the differential heats of adsorption (see, e.g., [8]) at first fall sharply, and the further filling of the surface then occurs very slowly. Although it is impossible to pass quantitatively from such a curve to the distribution function with respect to values of local adsorption energies, this is again a qualitative indication that over the main part of the surface the value of ϵ changes very little.

3. Analysis of the characteristic curves led Radushkevich [10] to the conclusion that active carbons, with respect to the dimensions of "elementary adsorption volumes" form extremely monodisperse systems. It appears to us that this conclusion is also in accord with the idea that over the main part of the surface the value of ϵ changes to an inappreciable extent.

It is to be regretted that there are practically no reliable experimentaldata on the adsorption of gas mixtures in the literature. In comparing, therefore, the results of the analysis made above with experiment, we are compelled to confine ourselves to our measurements [5,8] of the simultaneous adsorption of ethylene and carbon dioxide (at 25°)and of ethylene and propene (at 7° and 25°) on active carbon.

We will first point out that in all the systems studied the rule relating to rectilinear projection of the total adsorption isosteres on the plane $\underline{a}_1 = 0$ is closely obeyed. Fig. 3 shows families of such projections for the case of ethylene–propene. On this figure partial pressures of ethylene are plotted along the axis of abscissas and those of propene along the axis of ordinates. The full lines represent the projections of the total adsorption isosteres for 7°, and the broken lines – for 25°. The number against each straight line indicates the value of the total adsorption for the given isostere in millimoles per gram. From our point of view the fact of the linearity of these isosteres is a consequence of the fact that in the systems that we have studied the condition of Equation 21 was realized.

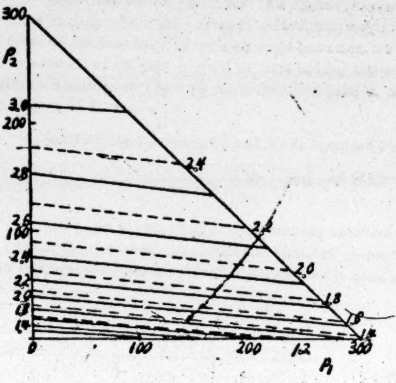

Fig. 3.

We will point out further that, as far as can be judged from the numerical data given in the paper of Lewis and coworkers [11] relating to the adsorption of binary gas mixtures, this rule applies also in the system studied by them. When this rule is obeyed, it is evidently very easy to construct the surface of total adsorption from the adsorption isotherms of the two pure components.

Contrary to the requirements of the approximate theory expounded above, the projections of the total adsorption isosteres are not parallel to one another. The absolute value of the slope of the experimental curve increases somewhat with rise in the degree of filling of the surface.

As was shown in our previous paper [8], the selectivity coefficient α_2 remains practically constant along each isostere, as required by the approximate theory given above; but it falls somewhat with rise in the degree of filling of the surface.

From the point of view presented in this paper, it is easy to understand the cause of the increase, with rise in degree of filling, of the slope of the projections of the total adsorption isosteres; and also the cause of the decrease in the selectivity coefficient α_2. Actually, the lower the degree of filling, the greater must be the effect of the adsorption sites having the greatest adsorption energies. It is clear from a comparison of Equations 10 and 16 that the absolute value of the slope of the projection of an isostere on the plane $\underline{a}_1 = 0$ must be the lower, the greater the effect of sites having high values of ϵ_2 (and therefore greater values of b_2).

Eliminating ϵ_2 from Equations 15 and 16, we find directly that sites having a higher value of ϵ_1 correspond to higher values of the selectivity coefficient α_2. With reduction in the degree of filling, therefore, the mean value of α_2 over the whole surface must increase.

The approximate statistical theory given in this paper for the adsorption of binary gas mixtures is therefore in good semiquantitative agreement with the results of experiment. At the same time this theory cannot yet give a quantitative solution of the problem formulated at the beginning of the paper, for it does not indicate a method of calculating the selectivity coefficient α_2. In this connection, let us examine, in conclusion, the question of the possibility of an approximate estimate of the value of this coefficient from Equation 15.

Starting from the concepts of the simplest adsorption scheme of Langmuir, we may write

$$\frac{b_{2s}}{b_{1s}} \approx \sqrt{\frac{M_1}{M_2}}\,. \qquad (22)$$

where M_1 and M_2 are the molecular weights of the adsorbed gases. As regards the value of $\epsilon_2 - \epsilon_1$, which enters into Equation 15, we may attempt to replace it approximately, for not too low degrees of filling, by the difference in the differential heats of adsorption q_i° of the two pure components at identical degrees of filling:

$$\epsilon_2 - \epsilon_1 \approx q_2^\circ - q_1^\circ \qquad (23)$$

There can be no doubt that this approximation is not particularly accurate, and it is permissible only in those regions where the curves of differential heats of adsorption against degree of filling have low slope. In favor of the soundness of such an approximation, we may argue that the difference $(q_2^\circ - q_1^\circ)$ automatically takes account of the part played by sites having higher values of adsorption energy, and that the use of this difference instead of $(\epsilon_2 - \epsilon_1)$ must therefore lead to the experimentally observed dependence of α_2 on the degree of filling.

Substituting Equations 22 and 23 in Equation 15, we obtain:

$$\alpha_2 \approx \sqrt{\frac{M_1}{M_2}}\, e^{(q_2^\circ - q_1^\circ)/RT}\,. \qquad (24)$$

Using the values of q_2° and q_1° that we obtained for the adsorption of pure ethylene and pure propylene on carbon [8], we have calculated the value of α_2 for the system in which we are interested from Equation 24. This calculation gives a somewhat unexpectedly good agreement with experiment, as will be seen from the table.

a_{12} (m-moles/g)	α_2 (Calcd)	α_2 (Found)
1.4	14.0	15.0
1.8	12.8	13.5
2.0	11.8	12.2

In spite of this agreement, we are not prepared to assert, as yet, that this method of calculation is of a sufficiently universal character.

The authors are deeply grateful to M. M. Dubinin and B. V. Ilyin, who have shown constant interest in this investigation and have helped us in many ways. The authors consider it their duty to acknowledge their indebtedness also to S. Z. Roginsky for interesting and fruitful discussion of the results given above.

SUMMARY

1. An examination has been made of the general equations yielded by the theory of the adsorption of binary gas mixtures on heterogeneous surface in absence of interaction.

2. An indication has been given of those cases in which it is possible to calculate adsorption from mixtures from the known isotherms for the adsorption of the pure components, without intermediate determination of the distribution function.

3. A rule has been deduced relating to the rectilinear character of projections of isosteres for total adsorption on the plane $a_1 = 0$, and the limits of applicability of this rule have been indicated.

4. A method has been given for the approximate evaluation of values of selectivity coefficients in those cases in which the rule of rectilinear isotherms of total adsorption holds.

5. A comparison has been made of the conclusions obtained with the results of an experimental investigation of the adsorption of binary gas mixtures on active carbon, and it has been shown that there is good agreement between theory and experiment.

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ELUCIDATION OF THE ROLE OF DIFFERENT ADSORPTION CENTERS IN THE HYDROGENATION OF ACETYLENE OVER NICKEL

COMMUNICATION 2. INVESTIGATION OF THE KINETICS OF THE HYDROGENATION AND ACTIVATED ADSORPTION OF ACETYLENE AT A NICKEL CATALYST

N. P. Keier

In the first communication [1] we gave the results of an investigation of the active surface of a nickel catalyst with the aid of a differential isotopic method. The nickel studied was prepared, following Bag and Egupov's method, by the alkali-leaching of a 50 % alloy of nickel with aluminum. Powerful activated adsorption of acetylene on the catalyst was observed at room temperature. A considerable part of the acetylene was adsorbed irreversibly, i.e. could not, under any conditions, be removed from the surface as acetylene. When the temperature was raised to above 150°, apart from acetylene, appreciable amounts of hydrogen and methane were desorbed.

It was established, with the aid of the differential isotopic method, that the active surface was heterogeneous with respect to activation energies for acetylene desorption. Catalytic reactions of different types occur on active adsorption centers differing in heats of adsorption and activation energies. The hydrogenation reaction is effected only on a small group of adsorption centers occupying 4-6% of the surface, and these adsorption centers comprise a part of those on which reversible adsorption occurs. Methane formation occurs at active centers corresponding to a lower degree of filling, i.e. having higher heats of adsorption and lower activation energies. Decomposition of acetylene with separation of hydrogen and formation of a surface compound of the nickel carbide type occurs in the case of acetylene adsorbed on more active centers.

Investigation of the catalyst after several adsorption experiments with the aid of X-rays* showed that it contains, apart from metallic nickel and residual aluminum oxide Al_2O_3, some nickel carbide Ni_3C [2], formed by reaction of acetylene with nickel.

In view of the established heterogeneity of the active surface, it was considered to be of interest to investigate the distribution of active centers according to their activation energies for the adsorption of acetylene and to determine the way in which the activation energy depends on degree of filling.

1. Determination of the Distribution Function for Active Adsorption Centers according to Activation Energies for the Adsorption of Acetylene

In order to find the distribution function with all its associated constants, and also to find the variation in activation energy, measurements must be made of at least two kinetic isotherms at two temperatures [3].

Repeat experiments on the adsorption of acetylene on the same sample of catalyst never gave agreeing results. Fig. 1 shows kinetic adsorption curves for a series of successive experiments on one sample of catalyst. Between the experiments, activation by prolonged degassing at 10^{-5} mm Hg and 300-500° was carried out. As will be seen from the graph, adsorption at a freshly activated surface is more than 2.5 times that found in all succeeding experiments (Fig. 1). Increase of activation temperature to 500° did not improve the reproducibility of the active surface. Progressive poisoning of the catalyst occurred in the successive experiments.

The graphs in Fig. 1 show that the kinetic adsorption isotherms satisfy the equation previously found for the adsorptions of many gases on various carbons, on nickelous oxide, and on other catalysts:

$$q = At^{1/n} \tag{1}$$

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* I take the opportunity of expressing my deep gratitude to M. Ya. Kushnerov for carrying out the X-ray investigation of the sample.

where

$$1/n = \alpha RT, \qquad (2)$$

and

$$A = \frac{H}{\alpha(\tau_0)^{\alpha RT}} \,. \qquad (3)$$

α and H are constants characterizing the distribution of active sites according to activation energies: $\rho(E) = He^{\alpha E}$ (4). As will be seen from Fig. 1, when several adsorption experiments are carried out on the same sample, poisoning is observed that has little effect on the slope of the curve representing the kinetics of adsorption in bilogarithmic coordinates. In Table 1 the values of log A and α for these experiments are given. It can be seen that α increases for a poisoned surface (in comparison with the first experiment), and then undergoes little change. H falls with poisoning. The absence in these experiments of an obvious relationship between changes in α and in A indicates that the fall of A is related to the fall in H. As it was impossible to carry out two reproducible experiments on the same sample, it was necessary to use a fresh sample of catalyst for each experiment. Identity of all conditions in the experiments was an essential prerequisite for the obtaining of reproducible results. Samples of 0.5 g were taken. The nickel was first dried for one hour at about 130-150° in a stream of nitrogen. The activation in these experiments was carried out under strictly constant conditions. The sample was degassed at 10^{-4} mm Hg at 300° for two hours, with a trap immersed in liquid nitrogen attached. Then, at the same temperature, the nickel oxides formed on the surface were reduced with hydrogen. At the end of the reduction process hydrogen was pumped off, the trap was removed for a period of 20 minutes from the liquid air in order to remove the water that had condensed, and it was then placed in solid carbon dioxide. The final degassing of the catalyst was carried out at 500° under the vacuum from a mercury condensation pump for one hour. Fig. 2 shows two kinetic adsorption isotherms obtained at 0° and 19.5° at the same pressure.

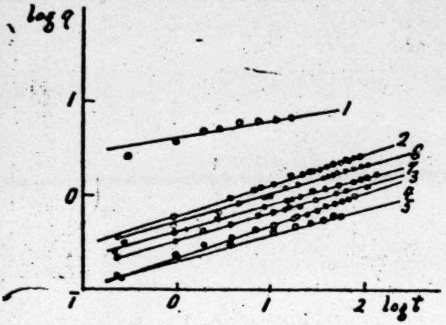


Fig. 1. Kinetics of the adsorption of acetylene in bilogarithmic coordinates log q and log t: 1) Expt. 1, freshly activated sample; 2) Expt. 2, sample from Expt. 1 activated at 360°, 10 hrs; 3) Expt. 3, same sample activated at 350°, 1.5 hrs; 4) Expt. 4, same sample activated at 350°, 1 hr; 5) Expt. 5, same sample activated at 350°, 1 hr; 6) Expt. 6, same sample activated at 500°, 1 hr; 7) Expt. 7, same sample activated at 500°, 1 hr.

The constants characterizing the kinetic curve, which are found from the slopes of the kinetic curves in bilogarithmic coordinates, are given in Table 2.

From the displacement of the kinetic isotherms measured at 0° and 19.5° along the coordinate RT log t, the constant log τ_0 was determined (−9.75). With the aid of the constants α, log τ_0 and A, the constants characterizing the distribution function of active centers according to their activation energies for the adsorption of acetylene were found [4]. The complete form of the distribution function is expressed by the equation

$$\rho(E) = 2.13\cdot10^{-12}e^{3.30\cdot10^{-4}E}\,(\text{cal/mole})^{-1} \qquad (5)$$

The variation in activation energy with the adsorption, found from Roginsky's equation [3], is given in Fig. 3. The activation energy rises from 11 to 18 kcal/mole when adsorption changes from 0.256 to 2.56 ml/g.

TABLE 1

Expt. No.	Pressure (mm Hg)	Temp. (°C)	log A	α (cal/mole)$^{-1}$	Activation conditions
1	5.88	22.2	0.6	$2.8 \cdot 10^{-4}$	Freshly prepared sample degassed at 300° for 1 hr.
2	2.67	25.6	$\bar{1}.78$	$5.8 \cdot 10^{-4}$	At 360° for 10 hrs.
3	2.77	25.5	$\bar{1}.52$	$5.0 \cdot 10^{-4}$	At 350° 1.5 hrs.
4	2.67	25.9	$\bar{1}.37$	$5.7 \cdot 10^{-4}$	At 350° 1 hr.
5	2.84	25.7	$\bar{1}.30$	$4.0 \cdot 10^{-4}$	At 350° 1 hr.
6	2.77	25.5	$\bar{1}.72$	$5.0 \cdot 10^{-4}$	At 500° 1 hr.
7	5.39	25.0	$\bar{1}.62$	$4.7 \cdot 10^{-4}$	At 500° 1 hr.

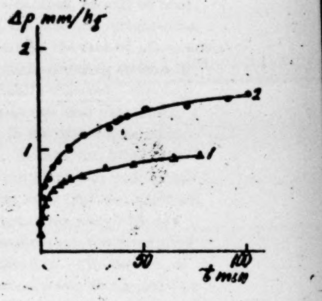


Fig. 2. Kinetics of the adsorption of, acetylene on a sample of previously dried nickel: 1) Expt. 8 (T 0°, P 4.478 mm Hg); 2) Expt. 9 (T 19.5°, P 4.355 mm Hg).

2. Comparison of the Rate of Adsorption of the Reaction Components with the Rate of Hydrogenation of Acetylene

There are indications in the literature that in a number of cases, in particular for the hydrogenation of ethylene on nickel, complete adsorption is a stage in which the active centers are removed from the catalytic reaction, and the hydrogenation reaction proceeds in the pre-adsorption state [5]. It was necessary to verify whether hydrogenation proceeds in our case by this mechanism as well as by the adsorption mechanism, for the hydrogenating group of active centers that we have found might then be only a small proportion of the catalytically active centers. Coincident or nearly coincident values of the initial rates of adsorption and hydrogenation would be an almost unequivocal proof of the presence of an adsorption mechanism, whereas a much higher value for the initial rate of hydrogenation would be evidence for the other mechanism.

TABLE 2

Expt. No.	Temp. (°C)	Pressure (mm Hg)	α RT	$\alpha \cdot 10^4$ (cal/mole)$^{-1}$	log A
8	19.5±0.1	4.55	0.25	4.37	−0.26
9	19.5±0.1	4.35	0.23	3.86	−0.26
10	0	4.48	0.21	3.85	−0.41
11	0	4.48	0.21	3.85	−0.41

In order to verify this hypothesis we have carried out experiments that permit an estimation of the rates of the initial stages of these processes. The initial rate of the process (expressed as the reduction in volume per minute per gram of catalyst) on admitting a mixture of acetylene and hydrogen (1:2) to freshly activated catalyst is 1.53 ml per min. per g (Expt. 18). The initial rate of adsorption of acetylene, also on a freshly activated nickel surface, is 1.57 ml per min (Expt. 19). The close values of the initial rates in these experiments, however, cannot be regarded as a proof of the adsorption mechanism of hydrogenation, for it was found that in Expt. 18, in addition to hydrogenation, there occurred also rapid irreversible adsorption of acetylene. In Expt. 18 the irreversible adsorption of acetylene amounted to 3.06 ml/g, and in Expt. 19, 2.55 ml/g was adsorbed at equilibrium. In order to estimate the true initial value of the rate of hydrogenation, comparative experiments were carried out on hydrogenation and adsorption over a sample of catalyst over which a preparatory adsorption of acetylene and hydrogen had been carried out, the sample being then degassed at room temperature, when a part of the reversibly adsorbed acetylene and hydrogen was removed from the surface.

In Fig. 4, Curve 1 represents the kinetics of the hydrogenation of acetylene in a 1:2 mixture at room temperature (Expt. 20, Table 3). After the hydrogenation the sample was again degassed at room temperature and adsorption of acetylene was allowed to occur on it (Expt. 21) at a pressure of 1.01 mm Hg, identical with the partial pressure of the acetylene in the hydrogenation experiment (Expt. 20). The kinetics of adsorption are represented by Curve 2 of Fig. 4. Comparison of the initial rates of the two processes shows that they are close in value. In the first five seconds, the pressure in Expt. 20 (on hydrogenation) fell by 0.26 mm Hg, and in one minute by 1.005 mm Hg. In the adsorption experiment, in the first five seconds the pressure fell by 0.326 mm Hg, and in one minute by 0.784 mm Hg. It will be seen that in this case the initial rate of hydrogenation

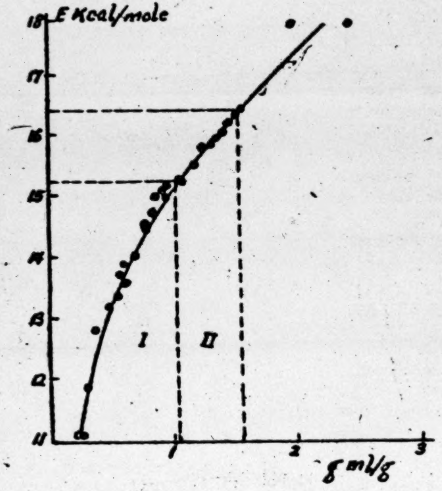


Fig. 3. Variation in activation energy of adsorption of acetylene with the degree of adsorption on a sample of previously dried nickel.

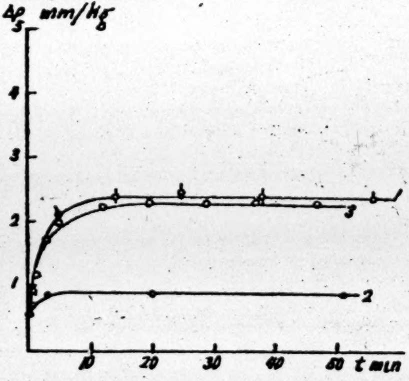


Fig. 4. Kinetics of the hydrogenation of acetylene expressed as the fall in pressure in the reactor per gram of catalyst: 1) Expt. 20, hydrogenation at room temp. on surface degassed after adsorption of acetylene at room temp.; 2) Expt. 21, adsorption of acetylene on sample from Expt. 20, degassed at room temp.; 3) hydrogenation at room temp. on the same sample degassed at room temp. after Expt. 18-21.

does not exceed the rate of adsorption. In the course of time, as will be seen from Fig. 4, the rate of hydrogenation begins to overtake the rate of adsorption, because the hydrogenating surface is being continually renewed. Slowing down occurs in this case only as the components in the original mixture are used up. In Expt. 20, altogether 61% of the acetylene was hydrogenated, the remaining acetylene was adsorbed. Of the hydrogen also, only 57% was used in hydrogenation, the remaining 43% being adsorbed. The amount of adsorbed hydrogen was about twice as great as in Expt. 18, in which adsorption of the hydrogen was carried out at a freshly activated surface under a pressure about three times as great as that of Expt. 20 (Table 3).

The incomplete utilization of acetylene for hydrogenation could result either owing to simultaneous adsorption of acetylene on centers inactive for hydrogenation, or at the end of the process, owing to insufficiency of hydrogen at hydrogenating centers (resulting from its more rapid adsorption). As the pressure of hydrogen in the mixture increases, the amount of adsorbed hydrogen increases (Table 5, Expts. 28-31) and that of acetylene falls, not however to zero. This fact is evidence that the process of the adsorption of acetylene proceeds simultaneously with hydrogenation at catalytically inactive centers, thus removing acetylene from reaction. Expts. 20, 28, and 29 show also that the rate of adsorption of hydrogen under these conditions is of the same order as that of the hydrogenation reaction. In experiments with 1:2 mixtures of acetylene and hydrogen, owing to the shortage of hydrogen due to its partial adsorption, there is an increased amount of adsorbed acetylene. Experiments 22-24 (Fig. 5, Table 3) show the effect of temperature on the rate of hydrogenation. It can be seen that there is no appreciable effect on the rate of the process resulting from rise in temperature up to 100°. With rise in temperature from 19° to 100° the amount of adsorbed acetylene falls from 37 to 25%, and that of hydrogen from 39 to 32%; the amount of hydrogenated acetylene rises from 61 to 70%. The residual pressure

TABLE 3

Expt. No.	Pressure of acetylene (P_g) (mm Hg)	Pressure of hydrogen (P_0) (mm Hg)	Temp. (°C)	Acetylene (mm Hg) hydrogenated	adsorbed	remaining	Hydrogen (mm Hg) hydrogenated	adsorbed	remaining
33	–	6.068	19	–	–	–	–	0.547	5.521
19	2.927	–	19	–	3.875	0.442	–	–	–
20	1.05	2.24	19	0.64	0.39	0.009	1.28	0.96	0
21	1.01	–	19	–	0.933	0.078	–	–	–
22	0.91	2.03	48	0.635	0.23	0.04	1.27	0.76	–
23	0.794	1.693	100	0.547	0.198	0.049	1.094	0.546	0.053
24	1.05	2.568	20	0.636	0.385	0.01	1.33	0.995	0.243
25	0.179	0.427	19	0.078	0.101	–	0.156	0.244	0.027
26	1.204	0.36	20	0.168	1.036	–	0.336	0.024	–
27	1.794	0.362	19	0.329	1.455	–	0.65	–	–
28	0.38	0.681	10	0.205	0.153	0.022	0.41	0.271	–
29	0.38	0.681	19	0.205	0.153	0.022	0.41	0.271	–
30	0.373	1.502	20	0.32	0.053	–	0.64	0.492	0.369
31	0.362	3.604	19	0.283	0.068	0.011	0.566	0.948	2.09

of acetylene and hydrogen rises (Expt. 23, Table 3). Increase in the partial pressure of acetylene (Expts. 25 and 26) lowers the degree of adsorption of hydrogen, probably owing to the rise in the rate of hydrogenation. When there is an excess of acetylene, a part of the hydrogen previously adsorbed on the surface is utilized.

The following conclusions can be drawn from this series of experiments: 1) hydrogenation of acetylene passes through the stage of complete adsorption; 2) in addition to hydrogenation, adsorption, which removes acetylene and hydrogen from the reaction, takes place (the adsorption of acetylene under these conditions is in accord with the fact that not all centers that reversibly adsorb acetylene are hydrogenating centers); 3) adsorption of hydrogen increases in presence of adsorbed acetylene; 4) the catalytic activity does not change in repeat experiments; 5) with rise in temperature, the minimum pressure of acetylene necessary for hydrogenation rises; 6) adsorption of hydrogen in presence of acetylene is higher than at a clean surface.

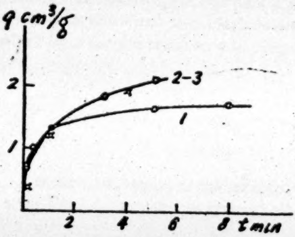


Fig. 5. Dependence of the kinetics of the hydrogenation of acetylene in a 1:2 acetylene – hydrogen mixture on temperature: 1) Expt. 23 (T 100°, P of mixture 2.487 mm Hg); 2) Expt. 22 (T 48°, P of mixture 2.94 mm Hg); 3) Expt. 20 (T 19.5°, P of mixture 3.29 mm Hg).

3. Discussion of Results

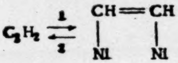
The results given in this communication taken together with those given in the first communication permit us to draw certain conclusions concerning the mechanism of the hydrogenation of acetylene and the formation of methane at a nickel surface.

a) Hydrogenation of Acetylene. As has been shown, the hydrogenation of acetylene passes through the stage of complete adsorption. Catalytic activity is confined to a small group of adsorption centers occupying about 4-6% of the surface. This group of active centers is characterized by definite values of activation energies and heats of adsorption. On a sample of low activity hydrogenation proceeds at active centers having activation energies of 15-16 kcal/mole; on an active sample the values are lower.

Experiments with the differential isotopic method have shown that hydrogenation proceeds on a fraction of the active centers on which reversible adsorption of acetylene occurs. The first hydrogenated portion of acetylene is in all cases close in composition to the first portion of acetylene desorbed at room temperature. This implies that hydrogenation occurs at a group of active centers having minimum, or almost minimum, activation energies for desorption (Fig. 6, shaded region bc). Hydrogenation does not occur at active centers having higher activation energies of adsorption.

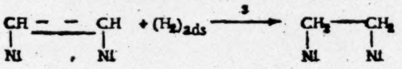
It might be supposed that one of the conditions for hydrogenation would be the geometric proximity of acetylene and hydrogen adsorption centers. Account must be taken also of the fact that in experiments in which hydrogen is adsorbed first and then the catalyst is brought into contact with acetylene, only a small amount of product, mainly ethylene, is formed. This is evidence that the mechanism of hydrogenation of adsorbed acetylene includes a stage of interaction with free hydrogen.

The mechanism of hydrogenation has been frequently discussed in the literature, mainly on the basis of the example of ethylene. The hydrogenation of acetylene is more complicated. We shall attempt to give a mechanism that will be consistent with our observations. The first stage is the reversible adsorption of acetylene with opening of one link and the weakening of a second:



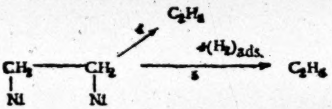
$$C_2H_2 \underset{2}{\overset{1}{\rightleftarrows}} \begin{array}{ccc} CH & = & CH \\ | & & | \\ Ni & & Ni \end{array} \qquad (1)$$

The second stage is the interaction of adsorbed acetylene with hydrogen adsorbed on neighboring active centers:



$$\begin{array}{ccc} CH & \overline{- \; -} & CH \\ | & & | \\ Ni & , & Ni \end{array} + (H_2)_{ads} \xrightarrow{3} \begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ Ni & & Ni \end{array} \qquad (2)$$

In this stage an intermediate complex is formed which corresponds to ethylene in composition. This complex may either be converted into ethylene and pass into the gas phase, or undergo further reaction with hydrogen adsorbed from the gas phase on a liberated active center:



$$\begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ Ni & & Ni \end{array} \overset{\nearrow^{4}\, C_2H_4}{\xrightarrow[5]{+(H_2)_{ads}}} C_2H_6 \qquad (3)$$

In our case, owing to the presence of an excess of hydrogen, Reaction 5 proceeds more rapidly than Reaction 4 and determines the ratio of ethylene and ethane. With rise in temperature, the rate of the back reaction (2) increases more rapidly than that of the forward one; for this reason the apparent temperature coefficient of the hydrogenation reaction is zero or even negative. It may be considered that the cause of the nonoccurrence of hydrogenation at some of the active centers that reversibly adsorb acetylene is the need for a definite degree of weakening in the double bond, which does not occur at the less active centers.

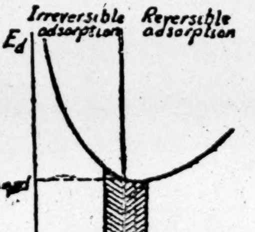
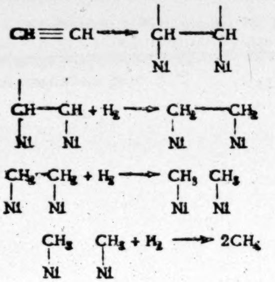


Fig. 6. Form of the curve for activation energy of desorption E_d against activation energy of adsorption: region ab) methane-forming centers; bc) hydrogenating centers.

b) Mechanism of the Formation of Methane. Formation of methane over the investigated catalyst occurs only above 150°. Formation of methane occurs both in presence of hydrogen on the gas phase, and also in its absence, owing to the redistribution of the hydrogen of the acetylene. By the use of labeled methane it was found possible to show that methane is formed on a definite group of active adsorption centers characterized by intermediate values of activation energy. Formation of methane occurs at active centers having lower E_{ads} values than those for centers at which reversible adsorption of acetylation occurs (see Fig. 6, shaded region ab).

The first stage of this reaction is the adsorption of acetylene. Being adsorbed on active centers differing in heats of adsorption, the acetylene molecules suffer internal bond breakdown in differing degrees. On active centers having low heats of adsorption and high energies of activation, the bond between the carbons of the acetylene molecule remains stronger than that between carbon and nickel atoms: on these active centers reversible adsorption of acetylene occurs. On active centers having higher heats of adsorption there are stronger bonds between carbon and nickel atoms, comparable with those between the carbons of the acetylene molecule. With increase in temperature, further strengthening of the bond between nickel and carbon occurs at these active centers, and it finally passes over into a carbide type of bond, the hydrogen being either adsorbed on neighboring active centers, or given up to the gas phase.

Reaction of the surface nickel carbide with hydrogen at a temperature of above 300° leads to the formation of methane. Formation of methane (also from adsorbed acetylene) at 150-200° proceeds by another mechanism on centers that are less active than those just discussed. We give below a scheme of processes leading to the formation of methane at this group of active centers:



$$\mathrm{CH{\equiv}CH \longrightarrow \underset{Ni}{\underset{|}{\overset{|}{CH}}}-\underset{Ni}{\underset{|}{\overset{|}{CH}}}} \qquad (1)$$

$$\mathrm{\underset{Ni}{\underset{|}{\overset{|}{CH}}}-\underset{Ni}{\underset{|}{CH}} + H_2 \longrightarrow \underset{Ni}{\underset{|}{CH_2}}-\underset{Ni}{\underset{|}{CH_2}}} \qquad (2)$$

$$\mathrm{\underset{Ni}{\underset{|}{CH_2}}-\underset{Ni}{\underset{|}{CH_2}} + H_2 \longrightarrow \underset{Ni}{\underset{|}{CH_3}}\ \ \underset{Ni}{\underset{|}{CH_3}}} \qquad (3)$$

$$\mathrm{\underset{Ni}{\underset{|}{CH_3}}\ \ \underset{Ni}{\underset{|}{CH_3}} + H_2 \longrightarrow 2CH_4} \qquad (4)$$

The first stage is the adsorption of acetylene on account of the breakdown of one of the π-bonds. A second bond then becomes unstable, and the state of the molecule approximates to that of a radical, so that hydrogen readily combines with it; evidence for this is to be found in the increased adsorption of hydrogen in presence of acetylene adsorbed on the surface. The second stage, therefore, occurs rapidly in presence of free or adsorbed hydrogen at room temperature. It should be noted that the high strength of the bond between carbon and nickel atoms at this group of active centers excludes the possibility of desorption of ethylene molecules from them. The third and fourth stages occur only at elevated temperature, for the action of hydrogen on adsorbed acetylene at room temperature does not lead to formation of methane. In absence of a supply of hydrogen from without, these reactions occur by the aid of hydrogen separating above 150° by the reaction:

$$3(\mathrm{C_2H_2})_{\mathrm{ads}} \longrightarrow 6\mathrm{Ni_3C} + 3\mathrm{H_2}. \qquad (5)$$

It is characteristic that methane and hydrogen always appear simultaneously in these experiments. The formation of hydrogen occurs, evidently, at the surface, and not in the gas space, for in our experiments the desorbed gas was removed from the reactor space into another space with the aid of a circulation pump so that the gas pressure above the catalyst during desorption did not exceed 10^{-4} mm Hg. Poisoning due to the adsorption process, which was observed after the first adsorption experiment, is probably associated with Reaction 5. The active surface is not restored by activation at 500°. This carbon is only partially removed in presence of hydrogen at temperatures of above 300° (in the form of methane). Methane formation was observed also in the repeat experiments, but on a reduced scale, thus indicating that, as a result of the reaction, methane-forming centers are freed. This is in accord with the proposed mechanism.

SUMMARY

1. Adsorption centers differing in their heats of adsorption and activation energies differ also in their catalytic properties. The hydrogenation and methane-forming reactions of acetylene occur at different groups of active centers, differing in their heats of adsorption and activation energies.

2. A mechanism has been proposed for hydrogenation in which the first stage is the reversible chemical adsorption of acetylene.

3. Methane formation occurs by two processes, one of which proceeds at a higher temperature via the reduction of a nickel carbide, and the other proceeds by the splitting of a partially hydrogenated adsorbed acetylene

molecule at the carbon —carbon linkage, followed by addition of a hydrogen molecule. The first process occurs at active centers having very high heats of adsorption, and the second occurs at active centers having lower heats of adsorption.

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SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 3. SOLUBILITY ISOTHERMS FOR THE TERNARY SYSTEM: $CO(NH_2)_2-H_2O_2-H_2O$

S. Z. Makarov and B. A. Lebedev

In 1875, Shene [1], professor at the Moscow Agricultural Academy, found that hydrogen peroxide can combine with a number of metal dioxides, forming double compounds, e.g. $K_2O_2 \cdot 2H_2O_2$, $BaO_2 \cdot 2H_2O_2$, etc. – the so-called perhydrates. Numerous investigators have since shown that compounds of this type are formed not only by metal peroxides, but also by many salts, weak bases, and certain organic compounds having the properties of weak bases. The study of compounds of this class proceeded, however, entirely by preparative methods. In the present investigation, unlike previous investigations (if we disregard that of Jänecke [2]), the conditions are determined for the synthesis of $CO(NH_2)_2 \cdot H_2O_2$ in the ternary system $CO(NH_2)_2-H_2O_2-H_2O$.

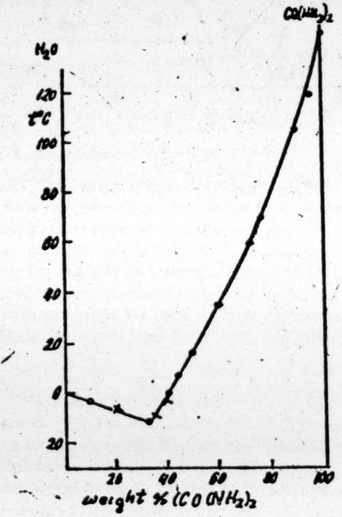

Fig. 1. The system $CO(NH_2)_2-H_2O$. o) Janecke's results; x) Blindin's results.

The binary system, $CO(NH_2)_2-H_2O$ has been studied by several authors [3,4,5,6,7] from 1902 onwards. The investigations of Jänecke [6] and Blindin [7] are the most interesting. Jänecke studied the course of the urea solubility curve, starting from the eutectic point and finishing with a solution containing 95% of urea. The eutectic of the system occurs at −11.5° at a concentration of 32.5% urea. The curve for the solubility of urea is featureless, thus indicating the absence of any hydrates or polymorphous modifications of urea. Blindin [7] found one point on the ice curve and two on the urea curve, thus permitting a determination of the position of the eutectic point, which was in good agreement with that found by Jänecke. Thus, these solubility data practically define the whole of the binary system $CO(NH_2)_2-H_2O$ over the whole concentration range of both components up to the melting point of urea, 132.5° (Fig. 1).

Information on the second binary system $H_2O_2-H_2O$ began to appear in the literature in 1900 [8,9,10,11,12,13]. In 1920 Maass and Herzberg [10] studied the liquidus line of the $H_2O_2-H_2O$ system by the visual method and showed that the chemical compound $H_2O_2 \cdot 2H_2O$ is formed. In 1940 Giguere and Maass [12] confirmed these results and supplemented them by a study of the solidus line; they showed that solid solutions were formed in the system by all the solid phases.

The fact that ice and hydrogen peroxide form solid solutions is in contradiction with the existing concepts concerning the possibility of forming solid solutions of ice. In 1950 Kubaschewski and Weber [13], in a more accurate determination of the transition points of this system with the aid of cooling and heating curves, determined the positions of the liquidus and solidus curves and confirmed Giguere and Maass's results concerning the presence in the system of pairs of solid solutions.

In February 1951, however, a paper appeared by Foley and Giguere [14] in which the existence of solid solutions of water in hydrogen peroxide and of hydrogen peroxide in water is completely rejected. The composition of the solid phases was determined by the method of the third indifferent component: potassium chloride. In order to prevent completely any possible displacement of the equilibrium between water and hydrogen peroxide owing to the presence of an appreciable amount of potassium chloride, the authors repeated their experiments, using the method of labeled atoms. As the third component they used radioactive phosphorus P^{32} (in the form of potassium dihydrogen phosphate KH_2PO_4), which in many respects was quite suitable for this purpose. The results of these experiments coincided with those previously obtained and confirmed the absence of solid solutions in the system $H_2O-H_2O_2$. Independently of this work, Mironov and Bergman [15], who determined cooling and heating curves by the visual method with great accuracy, also established the absence of solid solutions in this system (Fig. 2).

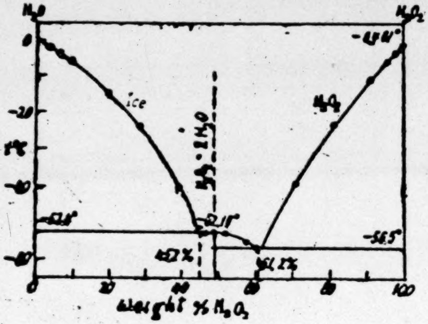

Fig. 2. Binary system $H_2O_2-H_2O$.

There are no data for the system $CO(NH_2)_2-H_2O_2$. Tanatar [16] first obtained the compound of urea with hydrogen peroxide $CO(NH_2)_2 \cdot H_2O_2$ in Russia in 1908. There is a wide patent literature on urea perhydrate and its preparation under laboratory and industrial conditions.

The ternary system $CO(NH_2)_2-H_2O_2-H_2O$ was investigated by Jänecke [2] in 1932 by the visual observation of the separation of the first crystals from aqueous solutions of urea and hydrogen peroxide in given proportions across sections of the ternary system. Jänecke took 11 sections with solutions of 3-92% of H_2O_2 and 5-60% of urea. From the results from these sections Jänecke constructed a diagram for the ternary system, predominantly in the ice and urea perhydrate regions, and partially in the urea region (Fig. 3). The results obtained by such a method make it possible to construct a diagram that is sufficiently accurate as a first approximation. The method chosen did not permit a direct determination of the composition of the liquid phase at the transition points of the system, and these points can therefore be considered to be known only approximately.

EXPERIMENTAL

We investigated the ternary system $CO(NH_2)_2-H_2O_2-H_2O$ by the isothermal method at three temperatures: 0, 5, and 10°. The procedure consisted in the preparation of a saturated solution which was in equilibrium at the given temperature with its corresponding solid phase, the permitted limits of temperature variation being $\pm 0.1°$. Equilibrium was established under good stirring in 1-4 hours, depending on the H_2O_2 content of the liquid phase. The criterion of the attainment of equilibrium was constancy of hydrogen peroxide concentration in two consecutive tests on the liquid phase.

Analysis of the liquid phase and the residue for hydrogen peroxide was carried out iodometrically, and urea was determined by conversion into ammonia followed by Kjeldahl distillation. The composition of the solid phases was determined graphically by the method of residues. The starting materials were urea of the firm of Schöring, carefully purified by recrystallization, and hydrogen peroxide completely freed from stabilizers and concentrated in a vacuum to an H_2O_2 content of 70-80%.

In experiments in which a greater concentration of hydrogen peroxide was required in the liquid phase we used urea perhydrate in place of urea, the perhydrate being prepared by the action of perhydrol on crystalline urea at 0°. This product, after being dried between filter papers in the air had practically the exact hydrogen peroxide content that is theoretically required for $CO(NH_2)_2 \cdot H_2O_2$. When kept for a long time in absence of stabilizer, it slowly decomposed, with separation of hydrogen peroxide, and deliquesced.

The results of the investigations of the ternary system for the three temperatures, 0, 5, and 10°, are shown in the table in the diagrams (Figures 4, 5, and 6).

TABLE

Results of the Investigation of the System $CO(NH_2)_2-H_2O_2-H_2O$ at 0, 5 and 10°

Point No.	Comp. of liquid phase (% by wt.)			Comp. of residue (% by wt.)			Solid phase
	$CO(NH_2)_2$	H_2O_2	H_2O	$CO(NH_2)_2$	H_2O_2	H_2O	
				t = 0°			
1	39.98	—	60.02	—	—	—	$CO(NH_2)_2$
2	38.07	3.00	58.93	79.33	0.76	19.91	$CO(NH_2)_2$
3	47.81	5.92	46.27	90.39	10.17	—	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
4	47.80	6.02	46.18	83.08	6.33	10.59	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
5	48.22	5.98	45.80	86.19	8.00	5.81	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
6	42.38	5.30	52.32	59.10	30.28	10.62	$CO(NH_2)_2 \cdot H_2O_2$
7	19.33	13.78	65.89	59.92	28.60	11.48	$CO(NH_2)_2 \cdot H_2O_2$
8	20.52	15.29	64.19	58.51	32.27	9.21	$CO(NH_2)_2 \cdot H_2O_2$
9	17.24	16.31	66.45	57.07	32.40	10.53	$CO(NH_2)_2 \cdot H_2O_2$
10	12.71	37.20	50.09	54.93	34.47	10.60	$CO(NH_2)_2 \cdot H_2O_2$
11	9.71	56.19	34.10	57.25	37.84	4.91	$CO(NH_2)_2 \cdot H_2O_2$
				t = 5°			
	44.0	0.0	56.00	from solubility diagram			$CO(NH_2)_2$
1	50.86	2.02	47.12	93.62	0.34	6.04	$CO(NH_2)_2$
2	51.96	6.27	41.77	—	3.67	—	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
3	51.22	6.28	42.50	90.1	4.98	4.92	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
4	28.04	12.61	59.35	58.02	29.56	12.42	$CO(NH_2)_2 \cdot H_2O_2$
5	15.94	18.98	65.08	53.00	32.23	14.73	$CO(NH_2)_2 \cdot H_2O_2$
6	14.36	27.27	58.37	60.22	34.16	5.62	$CO(NH_2)_2 \cdot H_2O_2$
7	9.22	62.73	28.05	40.40	37.63	11.07	$CO(NH_2)_2 \cdot H_2O_2$
				t = 10°			
1	47.88	—	52.12	—	—	—	$CO(NH_2)_2$
2	47.87	—	52.13	—	—	—	$CO(NH_2)_2$
3	51.84	5.79	42.37	77.18	2.94	19.88	$CO(NH_2)_2$
4	53.26	6.98	39.76	68.08	18.37	13.35	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
5	40.21	9.03	50.76	63.76	34.83	1.41	$CO(NH_2)_2 \cdot H_2O_2$
6	34.25	11.44	54.31	56.73	30.34	12.93	$CO(NH_2)_2 \cdot H_2O_2$
7	15.33	25.11	59.56	60.02	35.19	4.79	$CO(NH_2)_2 \cdot H_2O_2$
8	17.81	28.34	53.85	56.52	34.92	8.93	$CO(NH_2)_2 \cdot H_2O_2$
9	9.48	57.74	32.78	56.84	39.12	4.04	$CO(NH_2)_2 \cdot H_2O_2$
10	11.56	70.51	17.93	57.50	40.03	2.47	$CO(NH_2)_2 \cdot H_2O_2$

The solubility isotherms for the system $CO(NH_2)_2-H_2O_2-H_2O$ are characterized by the presence of two branches, corresponding to the equilibrium conditions for the solid phases $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$. Over the concentration range studied, up to 60-70% H_2O_2 in the liquid phase, no other urea compounds containing a greater amount of chemically combined hydrogen peroxide were detected.

Up to a content of approximately 5-7% H_2O_2, the solubility of urea rose to 48-54% along the branch corresponding to the conditions for the separation of $CO(NH_2)_2$. At higher concentrations of H_2O_2 the solubility of urea fell sharply, to approximately 10%, and the equilibrium solid phase became urea perhydrate $CO(NH_2)_2 \cdot H_2O_2$. The transition points on the isotherms corresponding to the presence of two solid phases

$$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2 ,$$

varied in composition to a comparatively insignificant extent over the temperature range studied.

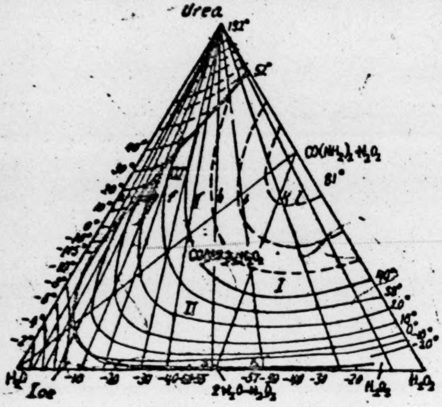
Urea
131°
52°
$CO(NH_2)_2 \cdot H_2O_2$
81°
$CO(NH_2)_2 \cdot 2H_2O_2$
I
II
40°
58°
20°
10°
0°
-10°
-20°
H_2O
Ice
-10
-20
-30
-40
-57
-50
-40
-30
-20
$2H_2O \cdot H_2O_2$
H_2O_2

Fig. 3. The ternary system $CO(NH_2)_2$–H_2O_2–H_2O (according to Jänecke).

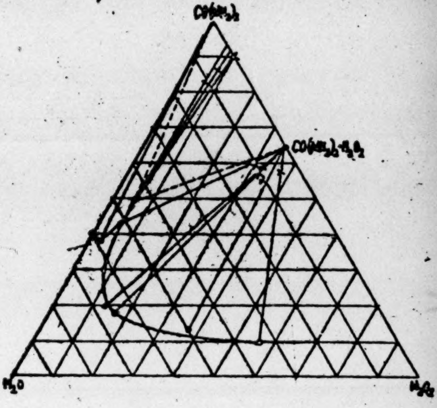
$CO(NH_2)_2$
$CO(NH_2)_2 \cdot H_2O_2$
H_2O
H_2O_2

Fig. 4. 0° Isotherm for the system $CO(NH_2)_2$–H_2O_2–H_2O.

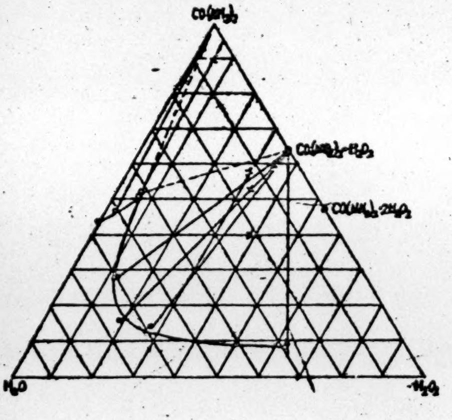
$CO(NH_2)_2$
$CO(NH_2)_2 \cdot H_2O_2$
$CO(NH_2)_2 \cdot 2H_2O_2$
H_2O
H_2O_2

Fig. 5. 5° Isotherm for the system $CO(NH_2)_2$–H_2O_2–H_2O.

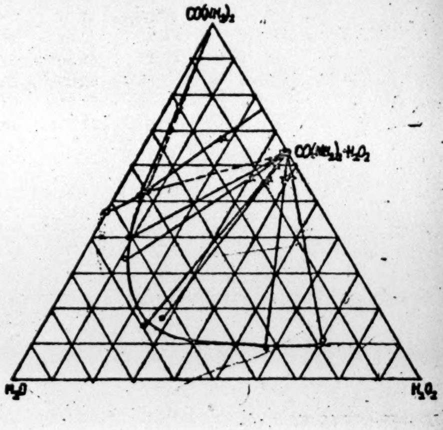
$CO(NH_2)_2$
$CO(NH_2)_2 \cdot H_2O_2$
H_2O
H_2O_2

Fig. 6. 10° Isotherm for the system $CO(NH_2)_2$–H_2O_2–H_2O.

	0°	5°	10°
$CO(NH_2)_2$	47.8	51.6	53.3
H_2O_2	6.0	6.3	7.0

The obtaining of solubility data for H_2O_2 concentrations in the liquid phase of higher than 70% presents certain difficulties: the solutions become unstable, and decomposition of hydrogen peroxide becomes appreciable.

When the isotherms obtained for 0, 5, and 10° are compared with data from Jänecke's isotherms, derived graphically from polythermal sections, discrepancies are clearly revealed. In the $CO(NH_2)_2$ and H_2O_2 concentrations Jänecke's isotherms fall appreciably behind those obtained by the isothermal method. It is clear that this phenomenon is due exclusively to the absence of true equilibrium, owing to the rapid crystallization of the solid phases on cooling solutions of urea and hydrogen peroxide in studies by the polythermal method.

SUMMARY

1. The system $CO(NH_2)_2-H_2O_2-H_2O$ has been studied by the solubility method at 0, 5 and 10°.

2. For H_2O_2 concentrations in the liquid phase of up to 70%, isotherms are characterized by the presence of two branches, corresponding to two solid phases: $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$.

3. Urea perhydrate $CO(NH_2)_2 \cdot H_2O_2$, so-called "solid perhydrol", contains about 17.0% of active oxygen and is congruently soluble in water. In a number of cases its aqueous solutions can be used as solutions of hydrogen peroxide.

4. On the branch for saturation with $CO(NH_2)_2 \cdot H_2O_2$ there is a characteristic sharp fall in solubility of urea from about 50 to about 10%. Hydrogen peroxide at concentrations of greater than 5-7% has a salting out action on urea.

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HYDRATED CALCIUM SILICATES

N. A. Toropov, A. I. Borisenko, and P. V. Shirokova

Hydrated calcium silicates have for a long time occupied the attention of investigators, and the search for rational methods for the preparation of these compounds has been the subject of a large number of investigations. The interest shown in these compounds results from a number of causes. First of all, study of the conditions of formation of hydrated calcium silicates may permit us to understand the very complex mechanism of the hydration of Portland cement, the main components of which are calcium silicates. A knowledge of the chemistry of hydration, which causes the setting and hardening of cements, is of interest to technologists of the cement and building industries. Not less important is a knowledge of the processes of formation of hydrated calcium silicates for deciding the question of the desirability of the micronization of cements, which is now generally considered to determine not only the periods of setting and hardening of cements, but also the final strength of the cement "stone". Finally, the development of methods of preparing hydrated calcium silicates has been directed toward a search for methods of manufacturing noncalcined cement. Such searches are based on the supposition that synthesized hydrated silicates after dehydration at comparatively low temperatures will not lose their ability to hydrate again.

The literature shows that two methods have been used for the preparation of hydrated calcium silicates: hydrothermal synthesis, and synthesis in which elevated pressures and temperatures are not used.

Among the earliest investigations devoted to the hydrothermal synthesis of hydrated calcium silicates was that of Daubrée [1], in which wollastonite was formed by heating calcium silicate glass with a small amount of water in a glass tube at 400°. Doelter [2] observed the formation of wollastonite from calcium bicarbonate and silica gel at 400-425°.

By heating a mixture of lime and amorphous silica with a small amount of calcium chloride at 470° for 48 hours, Schlapfer and Niggli [3] obtained hillebrandite $2CaO \cdot SiO_2 \cdot H_2O$. The heating was carried out in a silver crucible contained in a steel vessel. The authors observed the formation of hillebrandite at various ratios of calcium oxide to silica. There are no indications in the paper, however, of the yield of finished product.

In an investigation of the formation of hydrated calcium silicates from calcium oxide and finely ground quartz, Nagai [4] heated aqueous mixtures containing CaO and SiO_2 in the proportions 5:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:5 in nickel crucibles contained in an autoclave. Heating was carried out at temperatures in the range 133-212° for one to ten days. By the application of methods of chemical, microscopic, and in some cases, X-ray analysis, the author established that a six-day treatment in an autoclave of the most basic mixtures ($CaO : SiO_2$ = 5:1 and 3:1) at 212° led to the formation of a product of composition $2CaO \cdot SiO_2 \cdot H_2O$, similar in its properties to natural hillebrandite. At low temperatures, less basic mixtures gave a substance of composition $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (afwillite), and at higher temperatures, $CaO \cdot SiO_2 \cdot 0.25\ H_2O$ (xonotlite). The author gave also the results of a study of the reaction between calcium oxide and silica in a stream of superheated aqueous vapor mixed with air.

Vigfusson and coworkers [5] have synthesized hydrated calcium silicates by heating a mixture of calcium hydroxide with finely ground quartz sand in a platinum crucible in an autoclave at 170° in presence of a large excess of $Ca(OH)_2$. The hydrated silicate obtained, which had the composition $2.07\ CaO \cdot SiO_2 \cdot 1.24\ H_2O$, was compared with hydration products formed by the action of steam, in one case on cement mortar, and in another case pure dicalcium silicate. After removal of sand and lime from the cement mortar formed in this way, the sample had the composition $1.94\ CaO \cdot SiO_2 \cdot 1.14\ H_2O$. The X-ray photographs of these samples, like their optical properties, were similar to one another, but differed from those of natural hillebrandite. Repeat syntheses of hydrate calcium silicates in mixtures richer in lime ($CaO : SiO_2$ = 4:1) yielded a product which after removal of unchanged lime and silica had the composition $2.14\ CaO \cdot SiO_2 \cdot 1.42\ H_2O$ and gave an X-ray photograph differing from those of the previous samples. The authors established that the composition of the hydrated calcium silicate obtained depends not only on the conditions of synthesis, but also on the ratio $CaO : SiO_2$ in the mixture to be given the hydrothermal treatment.

Keevil and Thorwaldson [6] studied the action of saturated steam on tricalcium and β- and γ-dicalcium silicates, which were contained in platinum crucibles at 50 to 374°. Application of methods of chemical, microscopic, and X-ray analysis showed that after two weeks' treatment with steam at 170° both forms of dicalcium silicate gave identical crystalline products. Calcination of the hydrated dicalcium silicate gave β-$2CaO \cdot SiO_2$, not containing free lime. Treatment of tricalcium silicate with steam at 110° yielded the hydrated calcium silicate $2CaO \cdot SiO_2 \cdot H_2O$ and calcium hydroxide. At higher temperatures the authors observed the formation of fine-grain crystals of a material having refractions of Ng = 1.597 and Np = 1.589, no calcium hydroxide being eliminated. Characteristically, when this fine-grain material was dehydrated at 900°, free lime and β-dicalcium silicate were always formed.

In investigating the hydraulic properties of a clay-lime material that had been given a hydrothermal treatment, Budnikov [7] found that a hydrated silicate of composition $2CaO \cdot SiO_2 \cdot nH_2O$ was formed from kaolinite and calcium hydroxide roasted at 800-900°. According to this author's results, a hydrothermal treatment, particularly under pressure, considerably accelerates the process of forming $2CaO \cdot SiO_2 \cdot nH_2O$ and increases the strength of the product.

The review of the literature made by Steinour [8] concerning the system $CaO-SiO_2-H_2O$ shows that the synthesis of hydrated calcium silicates at ordinary temperatures and pressures is very difficult. It can be seen from this review that even in very recent papers very contradictory results are given. Thus some authors consider that, when silica gel and calcium hydroxide react under ordinary conditions, hydrated silicates of composition $CaO \cdot SiO_2 \cdot aq$, $3CaO \cdot 2SiO_2 \cdot aq$ and $2CaO \cdot SiO_2 \cdot aq$ are formed, the last compound being in equilibrium with a saturated solution of $Ca(OH)_2$. Other authors consider that only one compound of composition varying between $4CaO \cdot 5SiO_2 \cdot aq$ and $2CaO \cdot SiO_2 \cdot aq$ can exist in equilibrium with a saturated solution of calcium hydroxide.

As Mikhalchenko [9] showed, the rate of absorption of lime by silica at ordinary temperature and pressure depends to an appreciable extent on the degree of hydration of the silica. According to the author's results, more hydrated silica absorbs lime more readily than less hydrated silica does. The absorption of lime by silica is essentially a chemical process.

The investigation of the system $CaO-SiO_2-H_2O$ by Taylor [10] shows that the hydrated calcium silicates formed in the system are crystalline substances, and it confirms the results of electron-microscope observations that revealed the crystalline nature of hydrated silicates. Taylor submitted hydrated calcium silicates obtained by three different methods to X-ray analysis and showed them to be identical. In spite of great care in carrying out the experiment, the author had great difficulty in obtaining reproducible results. The most recent investigations [11] give us reason to believe that the most probable cause of the poor reproducibility of results is the variation in dispersion of the silica particles.

This far from full review of the investigations shows that all the methods that have been applied for the synthesis of hydrated calcium silicates have given insignificant yields of ready products, have required a long time for the reaction in which the hydrated silicates are formed, and, what appears to be the most serious drawback, have demanded the introduction of a great excess of calcium hydroxide in order to yield hydrated silicates having a $CaO : SiO_2$ ratio of greater than unity.

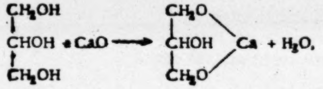
EXPERIMENTAL

Synthesis of Hydrated Calcium Silicates

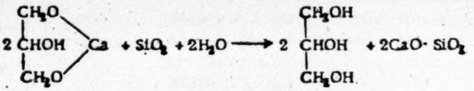
For the synthesis of hydrated calcium silicates we used the method of treating amorphous silica with a solution of calcium oxide. As Brauns [12] has pointed out, the method of preparing certain minerals by the action of solutions on solids was successfully applied already in the last century. The starting materials were calcium oxide obtained by the calcination of chemically pure calcium carbonate, and dehydrated amorphous silica. The calcination of calcium carbonate was carried out for one hour at 1000°, and the dehydration of amorphous silica for six hours at 500°. Chemical analysis showed that the CaO content of the calcined product was 99.71% and the SiO_2 content of the dehydrated amorphous silica was 99.86%.

Calcium oxide and amorphous silica taken in the necessary proportions were mixed in a porcelain mortar, and a small amount of glycerol dried at 160° was added immediately. The contents of the mortar were homogenized by prolonged grinding. The presence of glycerol during grinding was intended to prevent contact of the calcium oxide and amorphous silica with atmospheric carbon dioxide and moisture. After the grinding, the mixture was transferred to a 250 ml conical flask, into which sufficient glycerol was added to make its total amount up to 8-9 times the weight of the dry charge. The conical flask was then placed on an electric hotplate covered with a thin sheet of asbestos and was heated with continuous stirring at 180-185°. When this temperature was reached, the mixture began to froth. Froth formation was reduced by cutting down the supply of heat and shaking the flask; it stopped 3-3.5 hours after the attainment of the temperature of 180°, and the liquid in the flask became clear. Complete dissolution was an indication that the reaction leading to the formation of calcium silicate was complete. Heating was discontinued, and the contents of the flask were cooled to ordinary temperature and diluted with distilled water, when a white precipitate of hydrated calcium silicate came down. After twelve decantations, the precipitate was pressed off on a vacuum funnel, washed, first with distilled water and then with alcohol, and then dried for four hours at 100°. Precipitation of hydrated calcium silicate must be carried out only from cold solution, because the precipitate obtained by dilution of a hot solution settles slowly, and decantation is very prolonged.

When the mixture is heated, calcium oxide dissolves first with formation of calcium "glycerate":



and the glycerate reacts with silica with formation of calcium silicate:



On dilution of the cold solution and washing the precipitate, the hydrated silicate is formed:

$$2CaO \cdot SiO_2 + H_2O \longrightarrow 2CaO \cdot SiO_2 \cdot H_2O.$$

It was shown by heating a mixture of glycerol and dehydrated amorphous silica under these conditions that silicon dioxide is insoluble in pure glycerol. We may therefore consider that the dissolution of amorphous silica is the result of its reaction with calcium glycerate.

It should be noted that in the hydration process more than one molecule of water unites with one molecule of dicalcium silicate. However, drying of the hydrated product at 100° to constant weight followed by chemical analysis of the hydrated silicate obtained shows that one molecule of water is held fairly firmly.

For the synthesis of hydrated dicalcium silicate $2CaO \cdot SiO_2 \cdot H_2O$, which is of the greatest practical interest and which is prepared under hydrothermal conditions with the greatest experimental difficulties, we prepared the following charge:

Calcium oxide	4.21 g
Amorphous silica	2.25 g
Glycerol	60.00 g

In the whole series of experiments the product from the drying of the pressed and washed precipitate was a white stonelike material, readily ground in a mortar. An attempt to use the fraction of finely ground rock crystal passing through a sieve having 10,000 mesh per cm² did not give positive results. In this case the reaction of silicate formation proceeded very slowly, and the use of rock crystal, instead of amorphous silica was found to be inexpedient.

Investigation of the Products of the Synthesis

Chemical analysis of the hydrated silicate dried at 100° showed that the synthetic product was identical in composition with hydrated dicalcium silicate (Table 1).

The synthesized hydrated silicate could not be studied microscopically even at the greatest magnification, the particles being evidently so small that they appeared amorphous. X-ray* investigation, however, showed that

---

* The X-ray photograph was taken by Yu. G. Sokolov.

TABLE 1

Found in synthesized sample (%)				Calculated for $2CaO\cdot SiO_2\cdot H_2O$ (%)			
CaO	SiO_2	H_2O	Total	CaO	SiO_2	H_2O	Total
58.56	31.44	9.83	99.83	58.97	31.57	9.46	100.0

TABLE 2

Taylor's results		Found for $2CaO\cdot SiO_2\cdot H_2O$	
d/n	I/I_1	d/n	I/I_1
10.00	weak		
3.05	strong	3.053	10
2.80	strong	2.809	6
2.40	weak	2.412	2
2.20	very weak	2.211	1
2.10	very weak	2.109	1
2.00	medium	2.014	6
1.80	strong	1.810	9
1.55	weak	1.561	3
1.39	very weak	1.401	1
1.225	very weak	1.232	1
1.165	very weak	1.170	1
1.100	extremely weak		
1.045	extremely weak		

the hydrated silicate obtained had a crystalline character (X-ray photograph in cylindrical camera with $K_\alpha Co$ rays). Also, calculations from the X-ray photograph and comparison of the results of the calculations with those of Taylor [10], for samples of hydrated calcium silicate synthesized from tricalcium silicate and containing $CaO: SiO_2$ in the ratio 1.94:1, showed that the structures of the two materials were of the same type (Table 2).

Microscopic investigation of the hydrated silicate after being dehydrated by a two-hour calcination at 900° showed that it consisted of fine granular aggregates having the refraction values $Ng = 1.734$ and $Np = 1.718$. Calcination at the same temperature for four hours encouraged the growth of the grains of dicalcium silicate, without changing the values of the refractive indices. There was no free lime in the dehydrated preparation.

SUMMARY

1. Calcium "glycerate" reacts with amorphous silica with formation of dicalcium silicate, readily isolable from the glycerol solution by dilution, when it is obtained in the form of a hydrated silicate of composition $2CaO\cdot SiO_2\cdot H_2O$.

2. The proposed method permits the preparation of dicalcium silicate without the introduction of excess of calcium oxide into the reaction mixture. The reaction between calcium glycerate and silica gives a 100% yield of dicalcium silicate. The hydrated calcium silicate obtained is a crystalline compound.

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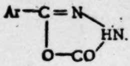
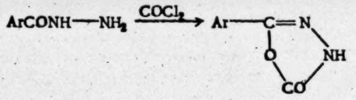
SYNTHESIS OF 5-ALKYL-1,3,4-OXADIAZOL-2(3H)-ONES AND STUDY OF THEIR REACTIONS WITH AMMONIA

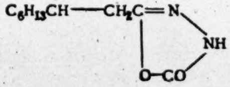
V. M. Rodionov and V. K. Zvorykina

In one of our previous communications [1] it was shown that, when Hofmann's reaction is carried out with amides of certain N-acylated β-aryl-β-amino acids, the final products include 5-substituted 1,3,4-oxadiazol-2(3H)-ones (I):  (I) The structures of these compounds were established by elementary analysis, by study of their properties and reactions, and also by confirmatory synthesis by Lieser and Nischk's elegant method [2]:



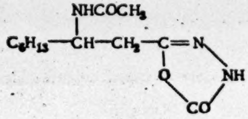
The study of oxadiazolone derivatives is of interest on its own account, and a more detailed investigation was therefore made of these compounds. The first experiments were carried out on 3-aminononanoic acid, which has already been well studied by us. As starting materials for the synthesis of these substances we prepared the hydrazides of the N-benzoyl and N-acetyl derivatives of 3-aminononanoic acid by heating their esters with hydrazine hydrate.

The hydrazides obtained were converted by a somewhat modified form of Lieser and Nischk's method (see Experimental) into 5-(2-benzamidooctyl)-1,3,4-oxadiazol-2(3H)-one (II) and 5-(2-acetamidooctyl)-1,3,4-oxadiazol-2(3H)-one (III):



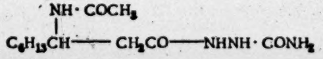
(II)

and



(III)

A number of interesting observations were made when attempts were made to convert the hydrazides of β-amino acids into semicarbazides by treatment with potassium cyanate. Thus the hydrazide of 3-acetamidononanoic acid reacts fairly smoothly (66% yield) with KCNO, giving the corresponding semicarbazide derivative (IV):



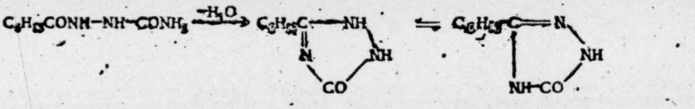
$$C_6H_{13}\overset{NH\cdot COCH_3}{\overset{|}{CH}}-CH_2CO-NHNH\cdot CONH_2$$

(IV)

In the analogous reaction with the hydrazide of 3-benzamidononanoic acid, a substance of acidic nature, m.p. 166°, was isolated; its structure has not yet been established.

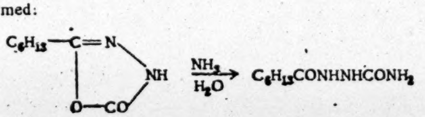
Treatment of the hydrazide of heptanoic acid with potassium cyanate yielded two compounds: one of a neutral character, m.p. 173°, corresponding in analysis to 1-heptanoylsemicarbazide $C_6H_{13}CONHNHCONH_2$, and a second of an acidic character, m.p. 167°. The latter substance corresponded in elementary analysis to the semicarbazide derivative + one molecule of water. A mixed test of the two did not give a depressed melting point (sharp melting at 173°). It was later found that the products are mutually interconvertible. Thus, when the substance of m.p. 167° is submitted to a long drying process (at a temperature of not above 100°), it loses the ability to dissolve in alkalis and is converted into 1-heptanoylsemicarbazide. On the other hand, the latter, on being recrystallized from water, melts, after drying in a desiccator, at 167°, acquires acid properties, and dissolves in alkalis. The mechanism of the mutual conversion of these compounds has not yet been established.

When the semicarbazide derivative is heated with a 10% solution of caustic potash, it loses one molecule of water, yielding 5-hexyl-1H-1,2,4-triazol-3(2H)-one [2]:

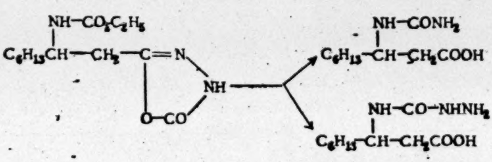


In the chemical literature there are differences in interpretation with respect to the structures of certain triazolones. Thus, Girard [3] considers that the triazolone compounds obtained by oxidation of semicarbazones of α-keto acids with iodine have the oxo structure; on being heated with alkalis they pass into hydroxy compounds. Compounds of the two types have sharp melting points and different properties. Unlike Girard, Gehlen [4] asserts that in this reaction cyanhydrazides are formed, and he proves this by synthesizing several of these compounds by the action of cyanogen bromide on hydrazides.

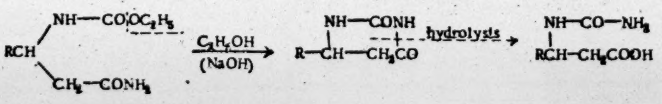
In connection with this conflict of evidence it was of interest to determine whether it is possible to convert oxadiazole compounds into triazole derivatives by treatment with ammonia. It is well known that certain 1,3-oxazine and γ-pyrone compounds fairly readily exchange O for NH. Such an attempt was made with 5-substituted 1,3,4-oxadiazol-2(3H)-ones, and it was found that, when 5-hexyl-1,3,4-oxadiazol-2(3H)-one is heated with alcoholic ammonia under a moderate pressure, scission of the five-membered ring occurs, and 1-heptanoylsemicarbazide is formed:



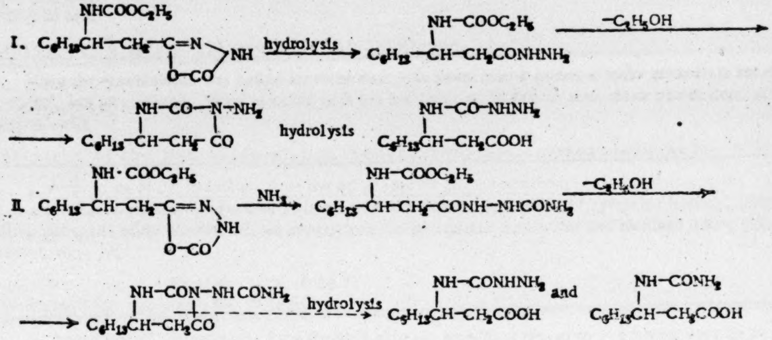
Extension of this reaction to 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one [2] led to the isolation of two substances: 3-ureidononanoic acid and 3-(3-aminoureido)nonanoic acid:



The unexpected formation of these compounds, especially the second, could be explained only by the intermediate formation of a hexahydropyrimidine ring and its subsequent hydrolysis, in a manner similar to that of the reaction that we have studied [5], in which amides of N-ethoxycarbonyl derivatives of β-amino acids are converted into β-ureido acids according to the following equations:



A similar explanation may be proposed also for the formation of 3-(3-aminoureido)-nonanoic acid by the reaction of ammonia with 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one. In this case the reaction mechanism is somewhat more complex and may be presented in two ways:



In both cases a hexahydropyrimidine derivative is formed intermediately, and it is then split up with formation of the β-(3-aminoureido) acid. The latter compound is of an amphoteric nature, dissolving both in dilute mineral acids and in alkalis; it is readily soluble in hot water, poorly soluble in cold water, and insoluble in organic solvents.

EXPERIMENTAL

Preparation of 5-(2-Benzamidooctyl)-1,3,4-oxadiazol-2(3H)-one

The hydrazide of 3-benzamidononanoic acid was prepared by heating an alcoholic solution of the ethyl ether of 3-benzamidononanoic acid for 36 hours with three times its amount of hydrazine hydrate; it crystallized from aqueous alcohol in colorless needles, m.p. 156-157° (yield 81%). The hydrazide of 3-benzamidononanoic acid (2 g) was heated in an oil bath for one hour at 120° and two hours at 150° with 40 ml of a 10% solution of $COCl_2$ in toluene. The excess of toluene and $COCl_2$ was driven off under a vacuum. The residue (1.69 g, 77%), a hard white mass, was recrystallized from aqueous alcohol, yielding fine colorless prisms, m.p. 126°.

Found %: C 63.95; 62.83; H 6.73; 6.84; N 13.72; 13.71
$C_{17}H_{23}O_3N_3$. Calculated %: C 64.35; H 7.25; N 13.25

Preparation of 5-(2-Acetamidooctyl)-1,3,4-oxadiazol-2(3H)-one

The hydrazide was prepared by heating 3-acetamidononanoic acid in alcoholic solution for 36 hours with three times its amount of hydrazine hydrate; colorless needles (from water), m.p. 165°, yield 64%. The hydrazide of 3-acetamidononanoic acid (2 g) was heated in an oil bath with 40 ml of a 10% solution of $COCl_2$ in toluene; one hour at 120°, and two hours at 150°. The excess $COCl_2$ and toluene were driven off under a vacuum. The solid product obtained was treated with 10% KOH, the alkaline solution was extracted with ether, the extract was filtered from some foreign matter, and it was then acidified with HCl. The white crystalline precipitate that formed was filtered off, washed with water, and recrystallized from water (1.72 g, 77.5%): long colorless needles, m.p. 116°.

Found %: C 56.95; 57.19; H 8.35; 8.57; N 16.90; 16.97
$C_{12}H_{21}O_3N_3$. Calculated %: C 56.5; H 8.2; N 16.5

Preparation of 5-Hexyl-1,3,4-oxadiazol-2(3H)-one from the Hydrazide of Heptanoic Acid.

The hydrazide was prepared by heating ethyl heptanoate in alcoholic solution for 36 hours with a threefold excess of hydrazine hydrate; it crystallized from water as colorless needles, m.p. 82°.

Found %: N 19.67; 19.70
$C_7H_{16}ON_2$. Calculated %: N 19.44

The hydrazide of heptanoic acid (1.3 g) was heated for two hours at 120-150° with 60 ml of a 10% solution of $COCl_2$ in toluene. The excess of $COCl_2$ and toluene were driven off under a vacuum, and the residue was distilled at 24 mm, yielding 1 g (65%) of a liquid of b.p. 192-196°. A second fractionation yielded a fraction of b.p. 193-195°/24 mm. The 5-hexyl-1,3,4-oxadiazol-2(3H)-one previously obtained by Hofmann's reaction boiled at 184-186°/18 mm.

Hydrolysis of 5-Hexyl-1,3,4-oxadiazol-2(3H)-one

When the oxadiazolone was boiled for three days with water over a gauze, a white crystalline substance, m.p. 81-82°, was precipitated. When admixed with the hydrazide of heptanoic acid, there was no depression in melting point.

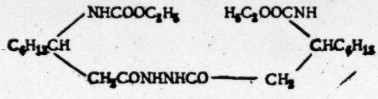
Preparation of the Hydrazide of 3-(Ethoxycarbonylamino)-nonanoic Acid

1. Preparation of the hydrazide from the ethyl ester of 3-(ethoxycarbonylamino)nonanoic acid. The ester (1 g) in alcoholic solution was heated for 15 hours with three times the amount of hydrazine hydrate. After distilling two-thirds of the alcohol off, we crystallized the precipitate from water and obtained 0.85 g (about 90%) of product, m.p. 142°.

Found %: N 16.46; 16.61

$C_{12}H_{25}O_3N_3$. Calculated %: N 16.21

2. Preparation of the hydrazide from the acid chloride by adding the latter in ethereal solution to a three-fold excess of hydrazine hydrate. The product was the diacylhydrazine:



Melting point after recrystallization from alcohol: 212°.

Found %: N 11.70 and 11.78

$C_{24}H_{44}O_6N_4$. Calculated %: N 11.52

Preparation of 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one from the Hydrazide

The hydrazide (0.8 g) was heated for 1.5 hours at 120-150° in an oil bath with a four-fold excess of a 10% solution of $COCl_2$ in toluene. The toluene was distilled off under vacuum, and the residue was treated with 10% NaOH. Acidification yielded a solution of 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one (0.7 g, 80%), m.p. 71-72°. In admixture with a sample (m.p. 73°) obtained by Hofmann's reaction, it melted at 72-73°.

Hydrolysis of 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one

A 20-hour boiling with water over a gauze yielded a precipitate from which a substance of m.p. 140-142° was isolated [in admixture with the hydrazide of 3-(ethoxycarbonylamino)nonanoic acid (m.p. 142°) it melted at 142°]. There was also a very small amount of a substance of m.p. 160°; in admixture with the amide of 3-(ethoxycarbonylamino)nonanoic acid it melted at 135-143°.

Preparation of the Ureide of 3-(Ethoxycarbonylamino)nonanoic Acid

The acid chloride obtained by heating 6.2 g of 3-(ethoxycarbonylamino)nonanoic acid with the theoretical amount of $SOCl_2$ at 40° was dissolved in 30 ml of absolute ether and added dropwise with cooling to double the amount of urea as a suspension in absolute ether. When the whole of the acid chloride had been added, the solution was stirred for a further two hours; the ether was driven off, and the residue remaining in the flask was heated in a boiling water bath for six hours. The product obtained was washed several times with ether, with 5% NaOH, and with water, and was recrystallized from 300 ml of alcohol. The ureide came down in the form of fine colorless needles, m.p. 198° (5 g, 66%).

Found %: N 14.80; 14.98

$C_{13}H_{25}O_4N_3$. Calculated %: N 14.63

The Action of Hypobromite on the Ureide of 3-(Ethoxycarbonylamino)nonanoic Acid

The ureide (5 g) was added under stirring over a period of two hours to a solution of hypobromite prepared at −5–10° from 1 ml of bromine in 30 ml of 10% NaOH. When solution was complete, the liquid was stirred for a further two hours, after which it was heated to 80° and cooled. On addition of HCl to a weakly alkaline reaction, an oil was precipitated. This crystallized out on the next day in clear colorless plates, m.p. 73°. In admixture with 3-(ethoxycarbonylamino)nonanoic acid (m.p. 79-80°) it melted at 60-62°. On further acidification to a weakly acid reaction, an oil was precipitated, from which, by treatment with bicarbonate, 3-(ethoxycarbonylamino)nonanoic acid was isolated together with some of the first substance, m.p. 73°. Further acidification yielded a precipitate of 3-(ethoxycarbonylamino)nonanoic acid. The products were: substance of m.p. 73° (1.82 g, 42%), which was 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one, and 3-(ethoxycarbonylamino)nonanoic acid (2.18 g, 43.6%).

Analysis of substance, m.p. 73°:

Found %: C 54.77; 54.99; H 8.38; 8.33; N 14.22; 14.29

$C_{13}H_{23}O_4N_3$. Calculated %: C 54.73; H 8.47; N 14.73

Preparation of 1-(3-Acetamidononanoyl)semicarbazide

KCNO (1 g) was added to 2 g of the hydrazide in 50 ml of water + 1 ml of concentrated HCl, and the solution was heated for two hours over a gauze. When the solution was cooled, a precipitate appeared, and this was filtered off, the filtrate being then evaporated down to low volume and again filtered. Altogether, 1.56 g (66%) of a substance giving melting points of 206° and 202° was obtained. After being recrystallized from water it was obtained as colorless plates, m.p. 212°.

Found %: C 53.03; 52.93; H 9.29; 9.20; N 20.5; 20.13

$C_{12}H_{24}O_3N_4$. Calculated %: C 52.9; H 8.82; N 20.51

Preparation of 1-Heptanoylsemicarbazide

KCNO (5.5 g) was added with cooling to a solution of 6 g of the hydrazide of heptanoic acid in 25 ml of water + 6.5 ml of 33% HCl. When the reaction mixture was heated, the precipitate that formed on addition of the cyanate went into solution; reprecipitation occurred when the solution was cooled. The precipitate was treated with 5% NaOH solution, and a part of it went into solution. When the alkaline solution was acidified, a white crystalline precipitate (0.2 g) separated; it was recrystallized from water and was found to melt at 167°. The alkali-insoluble part of the reaction product was also recrystallized from water and dried in a drying cabinet at 100°, yielding 5.7 g of fine needles melting at 173°. The first substance (m.p. 167°) was readily soluble in alkali and was precipitated from alkaline solution by acid; the second was insoluble. There was no depression in a mixed melting point (173°). The substance of m.p. 173° after being recrystallized from water and dried in a desiccator was found to melt at 167° and to acquire the ability to dissolve in alkalis, whereas the substance of m.p. 167° after long drying at 100° was found to melt at 173° and to have lost the ability to dissolve in alkalis.

Analysis of the substance of m.p. 173°:

Found %: C 51.59; 51.97; H 9.42; 9.26; N 22.58; 22.75

$C_8H_{17}O_2N_3$. Calculated %: C 51.33; H 9.09; N 22.46

Analysis of the substance of m.p. 167°:

Found %: C 46.08; 46.25; H 9.72; 9.60; N 20.34; 20.27

$C_8H_{17}O_2N_3 \cdot H_2O$. Calculated %: C 46.83; H 9.27; N 20.48

Preparation of 5-Hexyl-1H-1,2,4-triazol-3(2H)-one from 1-Heptanoylsemicarbazide

1-Heptanoylsemicarbazide (4.2 g) was heated at the boil over a gauze with 40 ml of 10% KOH. After 1 hour 30 minutes the solid present went into solution and did not separate when the solution was cooled. On acidification with HCl colorless needles (3.35 g) were precipitated. The melting point after recrystallization from water (300 ml) was 168.5°. It was readily soluble in caustic alkalis, being reprecipitated from solution by acid; it was insoluble in a solution of sodium carbonate or bicarbonate. In admixture with the substance of m.p. 167° from the preceding experiment it melted at 151-154°.

Found %: C 56.97; 56.87; H 8.74; 8.63; N 25.05; 25.17

$C_8H_{15}ON_3$. Calculated %: C 56.80; H 8.85; N 24.85

Action of Alcoholic Ammonia on 5-Hexyl-1,3,4-Oxadiazol-2(3H)-one

The hexyloxadiazolone (0.3 g) was heated in a sealed tube for three hours with 15 ml of an 8% alcoholic solution of NH_3. The alcohol was driven off, leaving a white crystalline substance. It melted, after recrystallization from water and drying on a water bath, at 171°. In admixture with 1-heptanoylsemicarbazide (m.p. 173°) it melted at 171-172°.

Action of Alcoholic Ammonia on 5-(2-Acetamidooctyl)-1,3-4-oxadiazol-2(3H)-one

The oxadiazolone derivative (0.5 g) was heated in a sealed tube for four hours at 120° and then 30 minutes at 140° with an 8% alcoholic solution of NH_3. The alcohol was distilled off, and the residue was dissolved in hot water. The solution was filtered from foreign matter and evaporated down, yielding a white crystalline substance of m.p. 160-180°. When this was treated with alcohol, a part went into solution. The residue melted, after being recrystallized from water, at 211°. In admixture with the previously obtained semicarbazide derivative (m.p. 212°) it melted at 211°. After removal of the alcohol by distillation and recrystallization of the residue from water, a hydrazide of m.p. 163° was obtained. In admixture with the previously prepared hydrazide of m.p. 165° it melted at 165°.

Action of Alcoholic Ammonia on 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one

5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one (0.5 g) was heated for three hours at 120° in a sealed tube with an 8% alcoholic solution of NH_3. After removal of alcohol by distillation, a crystalline substance of m.p. 117-120° remained. When this was recrystallized from water, two substances were obtained: one melting at 127-128°, and the other at 133-135°.

All the properties of the first compound, including its melting point, coincided with those of the 3-ureidononanoic acid previously prepared by us (in admixture, the two samples melted at 128°). The second compound was of an amphoteric character, being readily soluble in dilute mineral acids and caustic alkalis. After a double wash with ether and recrystallization from water, the melting point rose to 145° (with decomposition). In accordance with the elementary analysis of this compound we suggested that it was 3-(3-aminoureido)nonanoic acid, and this suggestion was confirmed by all further investigation. 3-(3-Aminoureido)nonanoic acid is readily soluble in hot water (colorless rhombic plates, sticking together by the side faces) and in alcohol; it is insoluble in ether and in benzene.

Found %: C 51.60; 51.41; H 9.00; 9.13; N 18.16; 18.33

$C_{10}H_{21}O_3N_3$. Calculated %: C 51.95; H 9.09; N 18.18

SUMMARY

1. The syntheses are given of several 5-alkylated derivatives of 1,3,4-oxadiazol-2(3H)-one, namely 5-(2-benzamidooctyl)-, 5-(2-acetamidooctyl)-, 5-hexyl-, and 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one.

2. It has been shown that, when 5-substituted 1,3,4-oxadiazol-2(3H)-ones are hydrolyzed, hydrazides of the original β-amino acids are formed.

3. It has been found that, when subjected to Hofmann's reaction, the ureide of 3-(ethoxycarbonylamino)-nonanoic acid also gives 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one.

4. The action of alcoholic ammonia on 5-substituted 1,3,4-oxadiazol-2(3H)-ones has been studied, and it has been found that in this reaction 5-hexyl- and 5-(2-acetamidooctyl)-1,3,4-oxadiazol-2(3H)-ones form 1-acylsemicarbazides derived from the corresponding β-amino acids.

5. When 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one is heated with alcoholic ammonia, it gives a mixture of 3-ureido- and 3-(3-aminoureido)-nonanoic acids. The mechanism of this reaction has been elucidated.

6. A study has been made of methods of preparing 1-(3-acetamidononanoyl)- and 1-heptanol -semicarbazides.

7. 1-Heptanoylsemicarbazide has been converted into 5-hexyl-1H-1,2,4-triazol-3(2H)-one.

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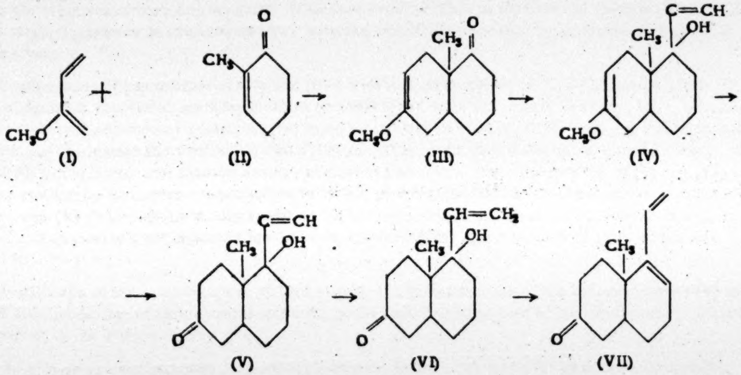
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVI. CONDENSATION OF 2-METHYL-2-CYCLOHEXEN-1-ONE WITH 2-METHOXY-1,3-BUTADIENE. SYNTHESIS OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE

I. N. Nazarov, L. V. Torgov, I. I. Zaretskaya, G. P. Verkholetova,
S. N. Ananchenko, and V. M. Andreev

In a previous communication [1] from our laboratory, we described the condensation of 2-methoxy-1,3-butadiene (I) with 2-methyl-2-cyclohexen-1-one (II). From the product, the hexahydromethoxymethyl-1(2H)-naphthalenone (III), we obtained some bicyclic alcohols (IV, V, and VI) and the hexahydromethylvinyl-2(1H)-naphthalenone (VII), which are important intermediate products for the synthesis of steroid compounds and related substances:

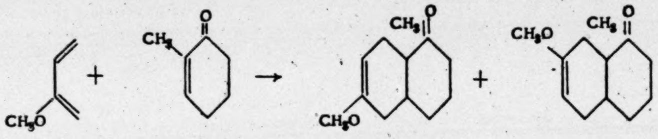


Condensation of the dienone (VII) with various dienophiles permitted the preparation of various polycyclic compounds, including, in particular, steroid tetracyclic diketones having hydrogenated cyclopentaphenanthrene and chrysene skeletons and containing angular methyl groups. Not all of these intermediate products, however, were prepared sufficiently smoothly and in satisfactory yield. In the present investigation, therefore, we have undertaken a detailed study of all stages of the preparation of the dienone (VII), and also of the possibility of improving the yields of all compounds required for its synthesis.

First of all, improvement was made in the method of preparing 2-methoxy-1,3-butadiene (I). It was found that consistent yields (75-80 %) of this diene were obtained by the splitting of methanol from 1,3,3-trimethoxybutane, not by means of freshly calcined potassium hydrogen sulfate, as recommended by Dikstra [2], but by the use of the residue from a previous experiment, containing potassium hydrogen sulfate mixed with organic substances. By this means it was found possible to obtain 2-methoxy-1,3-butadiene in a yield of 75-80%, instead of the 60-65% obtained by Dikstra's procedure.

A method was developed in detail also for the preparation of 2-methyl-2-cyclohexen-1-one (II) by the bromination of 2-methylcyclohexanone, as described in one of our communications. In the study of the condensation of 2-methoxy-1,3-butadiene (I) with 2-methyl-2-cyclohexen-1-one (II), the time and temperature of the reaction and the ratio of the components were varied. The best results were obtained with an eight-fold excess of the methylcyclohexenone at a temperature of 260-270° and condensation time of 2.5 hours. It was established also that additions of diethylaniline have a favorable influence. Under these conditions the yield of the hexahydromethoxymethyl-1(2H)-naphthalone (III) was 45-60%, reckoned on the methylcyclohexenone, and 27-29%, reckoned on the methoxybutadiene.

It was found that the condensation reaction goes in both of the theoretically possible directions, so that together with 2,3,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III), appreciable amounts (about 15%) are formed also of 2,3,4a,5,8,8a-hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalone (IIIa):



(I) (II) (III) (85 %) (IIIa) (15 %)

Owing to the closeness of their boiling points, it was not found possible to separate the isomers (III) and (IIIa), but the acetylenic hydroxy ketones (V) and (Va) prepared from them were readily separated by fractional crystallization.

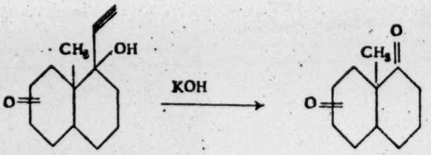
Condensation of the mixture of (III) and (IIIa) with sodium acetylide in liquid ammonia yielded a mixture of isomeric acetylenic methoxy alcohols (IV) and (IVa), from which only 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV) could be isolated in the crystalline form. It was later found convenient not to separate the methoxy alcohols (IV) and (IVa) in the pure state, but to convert them by the action of 1% hydrochloric acid into the hydroxy ketones (V) and (Va). From the mixture of (V) and (Va) it was found possible by fractional crystallization to isolate pure 5-ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V) in 40-46% yield, calculated on the ethynyloctahydromethoxymethylnaphthol taken. It was more difficult to isolate 8-ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va), which was obtained in 7-9% yield.

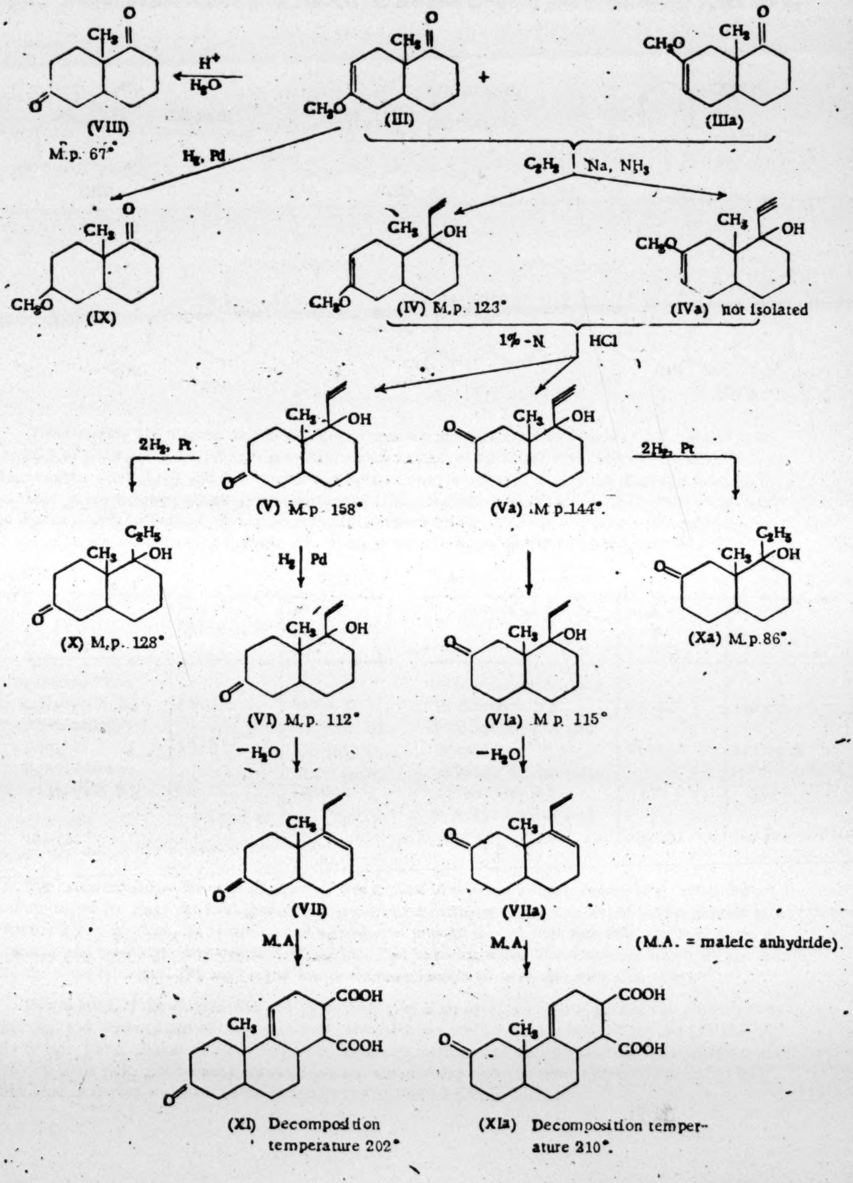
Distillation of the mother liquors yielded 15-20% of a liquid mixture of the hydroxy ketones (V) and (Va) and also, evidently, of their isomers, differing in the spatial arrangement of the substituents in position 1 with respect to the angular methyl group.

Exhaustive hydrogenation of the acetylenic hydroxy ketones (V) and (Va) gave the corresponding saturated hydroxy ketones (X) and (Xa). Selective hydrogenation of the acetylenic hydroxy ketones (V) and (Va) over a Pd catalyst gave the crystalline vinyl hydroxy ketones (VI) and (VIa). Dehydration of the latter with the aid of potassium hydrogen sulfate yielded the dienones (VII) and (VIIa). It should be noted that in the dehydration the conditions given in the Experimental part must be strictly observed, as otherwise not only does the yield fall, but the dienone itself becomes less active, possibly owing to transposition of double bonds.

The dienones (VII) and (VIIa) react in the cold with maleic anhydride, giving the corresponding condensation products. The reaction was complicated, however, by the formation of polymeric compounds, so that the yield of the acids (XI) and (XIa) was only about 10%. (See page 71).

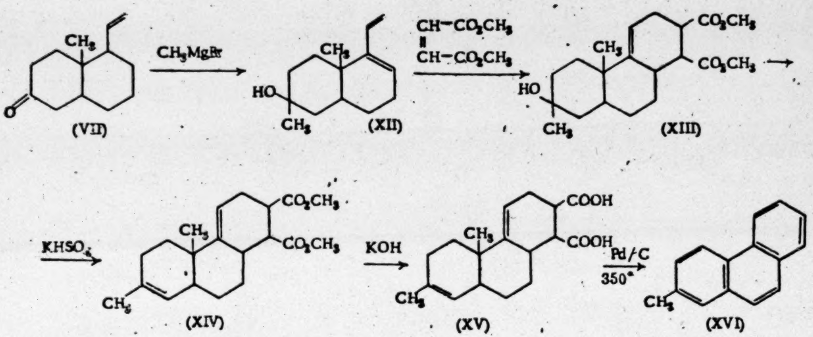
The obtaining of two series of isomers made it necessary to prove their structures, which has been done previously for the hexahydromethoxymethyl-1(2H)-naphthalenone (III) on the basis of model examples and analogies from the literature. It was at first proposed to convert each of the acetylenic hydroxy ketones (V) and (Va) into the corresponding diketones by the action of caustic potash according to the reaction:




(VIII)
M.p. 67°
H+
H2O
(III)
+
(IIIa)
H2, Pd
C2H2
Na, NH3
(IX)
(IV) M.p. 123°
(IVa) not isolated
1% -N
HCl
2H2, Pt
(V) M.p. 158°
(Va) M.p.144°.
2H2, Pt
(X) M.p. 128°
H2
Pd
(Xa) M.p.86°.
(VI) M.p. 112°
(VIa) M.p. 115°
−H2O
−H2O
(VII)
(VIIa)
M.A.
M.A.
(XI) Decomposition temperature 202°
(XIa) Decomposition temperature 210°.

(M.A. = maleic anhydride).

The diketones formed could be related by a series of reactions to well-known naphthalene hydrocarbons. Attempts at splitting the acetylenic hydroxy ketone by the action of caustic potash under various conditions did not, however, give a positive result: the hydroxy ketone was resinified, and the yield of diketone was negligible. Another method of proving the structure was therefore chosen: it may be represented by the scheme:



The dienone (VII) reacted with methylmagnesium bromide, giving a 90% yield of 1,2,3,4,4a,7,8,8a-octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). Condensation of the latter with dimethyl maleate yielded the dicarboxylic ester (XIII), which without being isolated, was dehydrated to give the dimethyl ester (XIV) of the decahydrodimethylphenanthrenedicarboxylic acid (XV). Hydrolysis gave the free acid (XV), which was dehydrogenated over palladium, giving 2-methylphenanthrene (XVI). The melting points of 2-methylphenanthrene itself and of its picrate coincided with the data given in the literature, as will be seen from Table 1.

TABLE 1

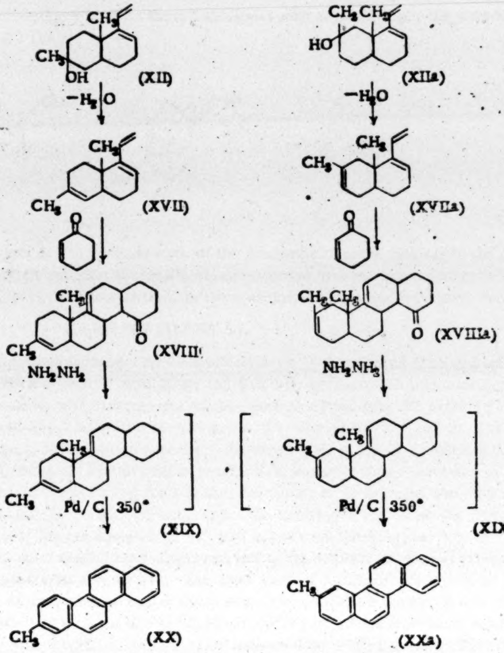
Substance	M.p. of hydrocarbon (°C)	M.p. of picrate (°C)
2-Methylphenanthrene (data in literature [3])	57-58	118-119
2-Methylphenanthrene (our results)	57-58.5	115-117
3-Methylphenanthrene (data in literature [4])	63	137-138

TABLE 2

Substance	M.p. of hydrocarbon (°C)	M.p. of picrate (°C)
2-Methylchrysene (data in literature [5])	229-230	143-146
2-Methylchrysene (our results)	222-223	145.5-146
3-Methylchrysene (data in literature [6])	170	164
3-Methylchrysene (our results)	166-169	160-161

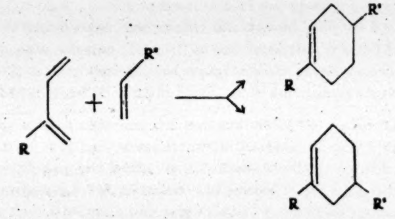
The same procedure for proof of structure was applied also to the hydroxy ketone (Va), but it did not yield definite results, since the final products, in particular 3-methylphenanthrene, could not be isolated in a pure form. It was, however, important to find a method of proving the structure that would be applicable to both isomers and would thus give comparable results. The following series of reactions, in which we successfully related the hydroxy ketones (V) and (Va) to known chrysene homologs, were therefore undertaken.

Dehydration of the dienols (XII) and (XIIa) with potassium hydrogen sulfate yielded the trienes (XVII) and (XVIIa), and condensation of these with 2-cyclohexen-1-one yielded the ketones (XVIII) and (XVIIIa) (in impure form). These substances were reduced by Kizhner's method, and dehydrogenation of the products gave 2-methylchrysene (XX) and 3-methylchrysene (XXa). The melting points of these hydrocarbons and of their picrates were in accord with data in the literature, as will be seen from Table 2.



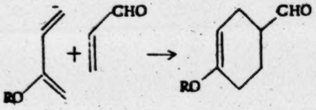
The structures of the dienones (VII) and (VIIa) and of all the associated compounds have therefore been rigorously proved.

The fact that in the diene condensation appreciable amounts (about 15%) of the 7-methoxy compound (IIIa) (meta isomer) were formed in addition to the 6-methoxy compound (III) (para isomer) deserves special attention. In the condensation of a 2-substituted butadiene with an unsymmetrical dienophile, two isomers may theoretically be formed:



Actually, Aschan [7] found, as long ago as 1928, that isoprene, when dimerizing, yields not only dipentene, but also the meta-isomer, diprene. Quite recently, Alder and Fogt [8] have shown that, when isoprene condenses with 3-buten-2-one or methyl acrylate, appreciable amounts (up to 15%) of meta-isomer are formed. In reactions, however, with 2-substituted butadienes having electronegative substituents (Cl, CN, OR, etc.), only para isomers have been isolated. Precisely similar results were obtained in the dimerization of chloroprene [9], 2-cyanobutadiene [10], 2-phenylbutadiene [11], 2-methoxy- and 2-formyloxy-butadienes [12], and also in the condensation of 2-phenylbutadiene with acrylic acid, acrolein, propiolic acid, and styrene [11].

In the condensation of 2-methoxy- and 2-ethoxy-butadienes with acrolein, only the para-alkoxytetrahydrobenzaldehydes were isolated [13]:



$R = CH_3, C_2H_5$

Our results, therefore, provide the first example of the formation of meta isomers in the condensation of 2-substituted butadienes in which the substituents are electronegative groups. Meta isomers are probably formed also in other cases, and only their low content in the reaction products has prevented their isolation.

EXPERIMENTAL

Preparation of 1,3,3-Trimethoxybutane. Nieuwland's catalyst [14], prepared from 4.5 ml of $BF_3 \cdot (C_2H_5)_2O$, yellow mercuric oxide (15 g), trichloroacetic acid (2 g), and absolute methanol (10 ml), was introduced into a three-necked two-liter flask provided with mercury-sealed mechanical stirrer, tube for passing gas, reflux condenser, and thermometer; and absolute methanol (480 g, i.e. 15 moles) was then added. The solution obtained was stirred for nine hours, during which gaseous butenyne (280 g, i.e. 5.4 moles) was passed; the temperature was maintained at about 40° by the heat of reaction (it was sometimes necessary to apply cooling). On the next day the reaction mixture was stirred for a further four hours at 35-40°, and was then cooled and neutralized with sodium methoxide (16 ml of a 6% solution). The unchanged methanol was distilled off under reduced pressure. Fractionation of the residue yielded 483 g of 1,3,3-trimethoxybutane, b.p. 60-62°/19 mm, n_D^{20} 1.4112. The methanol that had been distilled off (90-120 g) was again distilled at normal pressure, a further 15 g of trimethoxybutane being isolated from the residue. The total yield of 1,3,3-trimethoxybutane was therefore 498 g, i.e. 67% on the amount of methanol taken, or about 80% when recovered methanol was taken into account. It was found that, if a further addition of 1 ml of $BF_3 \cdot (C_2H_5)_2O$ and 5 g of mercuric oxide is made toward the end of the reaction (when it dies down), the yield can be further increased by 5-7%, but difficulties then arise in the fractionation of the product (violent bumping).

Preparation of 2-Methoxy-1,3-butadiene (I). Diphenyl ether (10 g) and finely ground potassium hydrogen sulfate (0.6 g) were placed in a three-necked 250 ml flask fitted with thermometer, dropping funnel, and efficient fractionating column. The mixture was heated to 150°, and 1,3,3-trimethoxybutane was added at such a rate that the temperature of the vapor leaving was maintained at not higher than 62°. A mixture of 2-methoxy-1,3-butadiene, 2,4-dimethyl-1-butene, and methanol distilled over. As more and more trimethoxybutane was added, the mixture in the flask became darker in color owing to resin formation, the amount of methoxybutadiene in the distillate increased, and the temperature of the vapor leaving fell to 58-69°. After the addition of the first 150 g of trimethoxybutane, the process was stopped, and the distillate was transferred to a flask containing 5% sodium carbonate solution (20 ml). It was found that it was better to treat the distillate obtained from the first 150 g of trimethoxybutane separately and to subject it to further treatment with potassium hydrogen sulfate, it being found to contain appreciable amounts of dimethoxybutene.

In this reaction it is necessary to take care that the temperature of the vapor leaving does not rise above 59°. At a given bath temperature, it is easy to regulate the temperature of the vapor by means of the rate of addition of trimethoxybutane (25-30 g per hour). It is desirable to carry out the reaction in a number of runs, interruptions being quite permissible. The distillate was washed twice with twice its amount of a 1% solution of sodium carbonate; it was then dried with calcium chloride (20-25% on the weight of methoxybutadiene) and distilled through an efficient column. The fraction of b.p. 72-75° and n_D^{20} 1.4430-1.4450 was collected; this was found to be quite suitable for further synthesis; the yield was 65-70%. The high-boiling fractions were submitted to further reaction, thus yielding a further amount of methoxybutadiene and increasing the total yield to 80%.

Preparation of 2,3,4a,5,8,8a-Hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III) and 2,3,4a,5,8,8a-Hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalenone (IIIa). 2-Methoxybutadiene (I) (15 g) and 2-methyl-2-cyclohexen-1-one (II) (120 g), prepared by the method described previously (b.p. 56°/9 mm, n_D^{20} 1.4865), were heated in a metal ampoule in presence of 1% of diethylaniline in an atmosphere of carbon dioxide for 2 hours 30 minutes, the bath temperature being 260-270°. The excess of methylcyclohexenone was driven off under reduced pressure (107 g). The residues from four identical experiments were united and subjected to three successive fractionations. The following fractions were obtained:

Fraction I, b.p. 73-90° at 13 mm; 10 g; n_D^{20} 1.4890

Fraction II, b.p. 60-90° at 1 mm; 16 g; n_D^{23} 1.5015

Fraction III, b.p. 90-100° at 1 mm; 43 g; n_D^{23} 1.5095

Fraction IV, b.p. 100-150° at 1 mm; 8 g; n_D^{18} 1.5135

Residue 35 g

Refractionation of Fraction (III) yielded 40 g of a mixture of the compounds (III) and (IIIa) having b.p. 92-96°/1 mm and n_D^{18} 1.5090. The yield was 44% on the methylcyclohexenone that reacted. Further fractionation of Fractions (II) and (IV) (united from many experiments) increased the yield of compounds (III) and (IIIa) to 50%. Numerous experiments were carried out under these conditions (about 150), and the yields were constantly reproduced: 27-29% on the 2-methoxybutadiene taken and 45-50% on the methylcyclohexenone that reacted. Reduction in duration of heating to 90 minutes and ten-fold dilution of the mixture had no appreciable effect on the yield. In this way about 1 kg of the hexahydromethoxymethyl-1(2H)-naphthalenones (III) and (IIIa) was obtained. The excess of 2-methyl-2-cyclohexen-1-one from 10-12 condensations was fractionated through a column in order to purify it, and it was then used again in the condensation reaction.

The semicarbazone of the hexahydromethoxymethyl-1(2H)-naphthalenone (evidently of III) is formed very rapidly when the compound is mixed with an alcoholic solution of semicarbazide acetate. It forms fine glistening crystals, m.p. 208-209.5° (from a mixture of dioxane and methanol).

Found %: C 62.1; 62.4; H 8.5; 8.2
$C_{13}H_{21}O_2N_3$. Calculated %: C 62.1; H 8.4

Hydrogenation of the Hexahydromethoxymethyl-1(2H)-naphthalenones (III) and (IIIa). The mixture of (III) and (IIIa) (6.1 g; b.p. 92-96°/1 mm, n_D^{21} 1.5090) dissolved in 10 ml of absolute dioxane was hydrogenated in presence of a Pd catalyst for 13 hours. The amount of hydrogen (20°, 760 mm) absorbed was 700 ml (770 ml was theoretically required). Vacuum fractionation of the product yielded 3.8 g of the corresponding octahydro-1(2H)-naphthalenone derivative (IX) having b.p. 89-91° at 0.5 mm; n_D^{23} 1.4892; d_4^{23} 1.039; found MR_D 54.5; calculated MR_D 54.9. The semicarbazone formed fine white crystals (from 70% alcohol), m.p. 199-202° (decomp.)

Found %: C 61.75; 61.8; H 9.3; 9.2
$C_{13}H_{23}O_2N_3$. Calculated %: C 61.65; H 9.15

In admixture with the semicarbazone of the original substance it melted at 186-192° (decomp.)

Preparation of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV). Liquid ammonia (300 ml) was introduced into a three-necked liter flask, provided with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene, and cooled with a mixture of solid carbon dioxide and methanol (−70°); sodium ([illegible] g) was added under stirring. Acetylene was passed at 20 liters per hour into the suspension formed, and after two hours a solution of 10.[illegible] g of the hexahydromethoxymethyl-1(2H)-naphthalenones (III and IIIa) in 60 ml of absolute ether was added over a period of ten minutes. Passage of acetylene was continued further for nine hours (2-3 liters per hour), the temperature being allowed to rise to −35°; finely ground ammonium chloride ([illegible]) was then added, and the mixture was set aside overnight. On the next day, water (100 ml) was added to the reaction mixture, which was then extracted three times with ether. The ether extracts were dried with magnesium sulfate and filtered, the ether was distilled off until crystals began to separate, and the mixture was then set aside overnight. On the next day the crystals were filtered off under suction and washed three times with a mixture of ether and petroleum ether. White crystals (2 g) of m.p. 121-[illegible] were obtained.

Crystallization from 5 ml of chloroform gave pure 1-ethynyl-[illegible]-methyl-1-naphthol (IV), m.p. [illegible] 123.5°.

Found %: C [illegible]6; 76.[illegible]; H 9.05; [illegible]
[illegible] Calculated %: C [illegible] H 9.15

The mother liquor from the first crystallization was evaporated and vacuum-distilled, yielding 6 g of a mixture of the methoxy alcohols (IV) and (IVa) in the form of a colorless liquid of b.p. 119-121°/1 mm and n_D^{21} 1.5263. Replacement of sodium by potassium or lithium in this synthesis did not give improved results.

Hydrolysis of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV) to Give 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V). A solution of 0.42 g of the ethynyloctahydromethoxymethylnaphthol (IV) in 5 ml of ether was shaken with 3 ml of 8% hydrochloric acid. Already after 20 minutes, white crystals began to precipitate. After two hours they were filtered off under suction, washed with ether and water, and dried in a desiccator. The product was 0.39 g of 5-ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V), m.p. 155-156°, which has been described previously [1]. The yield was thus almost quantitative.

Preparation of 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V) and 8-Ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va). Liquid ammonia (850 ml) was introduced into a 2-liter flask, provided with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene, and cooled with a mixture of solid carbon dioxide and methanol (−70°); sodium (17 g) was added under stirring. Acetylene (about 40 liters) was passed in the course of one hour, and the rate of passage was then reduced to 3-5 liters per hour. To the suspension of sodium acetylide formed, a solution of 80 g of the mixture of hexahydromethoxymethyl-1(2H)-naphthalenones (III and IIIa) in 250 ml of absolute ether was added over a period of one hour. Passage of acetylene (3-5 liters per hour) was continued for six hours, and the mixture was then set aside at −70° overnight. On the next day the mixture was stirred for five hours, acetylene being passed at 2-3 liters per hour and the temperature being allowed to rise to −35°. Finely ground ammonium chloride (60 g) was then added, a little at a time, and the mixture was then set aside overnight, the ammonia being allowed to evaporate away.

On the next day, ether (200 ml) was added, and the mixture was treated with ice water (80 ml). The ether layer was separated, and the aqueous layer was extracted three times with ether (150 ml altogether). The united ether extracts were evaporated down to a volume of 180-200 ml, 1% hydrochloric acid (100 ml) was added, and the mixture was stirred vigorously for three hours. Already after thirty minutes light-yellow crystals began to be precipitated. The precipitated crystals were filtered off under suction, washed four times with cold ether and twice with cold water, and dried to constant weight in a desiccator. The weight of hydroxy ketone (V) obtained in this way was 34-39 g (varying in different experiments); it melted at 154-155.5°, and was sufficiently pure for the subsequent hydrogenation treatment. A single crystallization from alcohol or benzene gave a product of constant melting point (158°).

Ether was removed from the mother liquor by distillation, petroleum ether was added, and the mixture was set aside overnight. By the next day crystals (6-8 g) had formed which consisted essentially of 8-ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va), m.p. 139-142°. Crystallization from alcohol yielded the pure isomer (Va), m.p. 144°.

Found %: C 75.9; 75.9; H 8.8; 8.9
$C_{13}H_{18}O_2$. Calculated %: C 75.7; H 8.8

The mother liquor after removal of solvents weighed 32-38 g, and on distillation it yielded 13-16 g of a liquid mixture of the hydroxy ketones (V) and (Va) having b.p. 134-136°/1.5 mm and n_D^{20} 1.5280. Analysis of this mixture of liquid hydroxy ketones gave the following results:

Found %: C 75.55; 75.5; H 9.15; 8.95
$C_{13}H_{18}O_2$. Calculated %: C 75.7 H 8.8

This mixture, like the pure hydroxy ketones (V) and (Va), gave a voluminous white precipitate with an ammoniacal solution of silver oxide (test for acetylenic hydrogen).

Exhaustive Hydrogenation of the Hydroxy Ketones (V) and (Va). The hydroxy ketone (V) (420 mg) dissolved in alcohol (5 ml) was hydrogenated in presence of platinum by Adam's method. Hydrogenation began immediately and was complete in 7 minutes, 100 ml (22°, 760 mm) of hydrogen being absorbed, as required by theory. The solution was filtered and allowed to evaporate. The readily soluble 5-ethyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (X) was isolated as white crystals (50 mg), m.p. 127-128°.

Found %: C 74.2; 74.0; H 10.7; 10.8

$C_{13}H_{22}O_2$. Calculated %: C 74.25; H 10.5

The hydroxy ketone (Va) was hydrogenated in a similar way, yielding 8-ethyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Xa) (0.6 g from 1.0 g of hydroxy ketone) in the form of white crystals, m.p. 86°.

Found %: C 74.2; 74.1; H 10.5; 10.4

$C_{13}H_{22}O_2$. Calculated %: C 74.25; H 10.5

In the hydrogenation of 2.1 g of the liquid mixture of hydroxy ketones, 465 ml (18°, 760 mm of hydrogen was absorbed, 460 ml being theoretically required.

Selective Hydrogenation of 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V) to Give Octahydro-5-hydroxy-4a-methyl-5-vinyl-2(1H)-naphthalenone (VI). The substance (V) (12.7 g) dissolved in 100 ml of dioxane was hydrogenated in presence of palladium carried on calcium carbonate until one molecule of hydrogen (1470 ml; 18°, 760 mm) had been absorbed. The solution was filtered, and the dioxane was driven off under reduced pressure. The light-yellow viscous mass that remained very slowly (after a week) crystallized out, but for the preparation of the dienone (VII) the product was used without being crystallized. The pure octahydro-5-hydroxy-4a-methyl-5-vinyl-2(1H)-naphthalenone (VI) melted at 111-112° (two crystallizations from petroleum ether). This alcohol has been previously prepared in our laboratory [1], but was then characterized as a liquid.

Selective Hydrogenation of 8-Ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va) to Give Octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa). The hydrogenation of the substance (Va) was carried out in a similar way. Crystallization was found to occur immediately after removal of solvent; 27.7 g of the alcohol (Va) yielded 19.6 g of crystals, m.p. 113-115°. The pure alcohol (VIa) melted at 114-115°.

Found %: C 75.15; H 10.1

$C_{13}H_{20}O_2$. Calculated %: C 75.0; H 9.7

Dehydration of Octahydro-5-hydroxy-4a-methyl-5-vinyl-2(1H)-naphthalenone (VI). A mixture of 16 g of the substance (VI), 8 g of finely ground potassium hydrogen sulfate, and 0.05 g of pyrogallol was heated at 140-145° for 30 minutes under reduced pressure (40-45 mm). The weight of water separated was 1.3 g (theoretical amount 1.4 g). The reaction mixture was cooled and extracted with ether; the ether was driven off, and the product was vacuum-distilled, yielding 10 g (67%) of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)naphthalenone (VII) in the form of a thick colorless liquid having a fairly pleasant odor. It boiled at 114-117°/3mm, or 100-103°/1mm, and had n_D^{18} 1.5260; d_4^{20} 1.022. The semicarbazone (from 80% alcohol) melted at 174.5-176°.

Found %: C 68.0; 68.15; H 8.8; 8.8

$C_{14}H_{21}ON_3$. Calculated %: C 68.0; H 8.6

Dehydration of Octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa). This dehydration was performed in the manner described above from 8.6 g of the substance VIa, the product being 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIIa) (5.9 g, 74%), which is a thick, colorless liquid having a fairly pleasant odor, b.p. 94-96°/0.5 mm, n_D^{18} 1.5270. The semicarbazone (from a mixture of methanol and dioxane) melted at 196-197°.

Found %: C 68.1; H 8.7

$C_{14}H_{21}ON_3$. Calculated %: C 68.0; H 8.6

Selective Hydrogenation of the Liquid Mixture of Acetylenic Hydroxy Ketones (V) and (Va). The substance (7.6 g) dissolved in alcohol (20 ml) was hydrogenated in presence of palladium carried on calcium carbonate until one molecule of hydrogen (840 ml, 18°, 760 mm) had been absorbed. The solution was filtered, and alcohol was distilled off under reduced pressure; the residue was diluted with ether (5 ml) and set aside at 0° to crystallize. After two months the mixture had partially crystallized out, and the crystals were pressed off under suction and washed with cold ether. The product was octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa) (1.7 g), m.p. 114-115°. In admixture with the sample obtained previously it showed no depression in melting point.

Dehydration of the Liquid Mixture of Vinyl Hydroxy Ketones. The mother liquor from the preceding experiment was dehydrated with the aid of potassium hydrogen sulfate, as described above, yielding 2.4 g (40%) of a mixture of the dienones (VII) and (VIIa), b.p. 114-119°/2 mm, n_D^{18} 1.5260.

Condensation of the Dienone (VII) with Maleic Anhydride. The dienone (VII) ([illegible]) was mixed with maleic

[illegible]

anhydride (0.4 g). Reaction set in very quickly, the temperature rising to 50°. The mixture was set aside for 12 hours, but crystallization did not occur, in spite of addition of solvent and cooling. Alcohol (3 ml) and 20% caustic potash (3 ml) were added to the mixture, which was then set aside for two hours. The homogeneous solution was diluted with an equal volume of water and extracted with ether, and the aqueous solution was acidified to Congo red with concentrated hydrochloric acid. A light-yellow sticky mass of polymer came down. The aqueous solution was decanted and set aside in the cold. Crystals (0.12 g) soon made their appearance, and they were recrystallized from 6 ml of 50% acetic acid, yielding 0.10 g of fine white crystals of the previously described [1] dicarboxylic acid (XI) which decomposes at 200-202.5° (rapid heating). Condensation in xylene at 140° gave similar results.

Condensation of the Dienone (VIIa) with Maleic Anhydride. In a similar way, the dienone (VIIa) (0.6g) yielded the dicarboxylic acid (XIa) (0.08g). On being heated rapidly, the acid melted with decomposition at 203°, but the material became transparent only at 210°.

Found %: C 66.3; H 7.3

$C_{17}H_{22}O_5$. Calculated %: C 66.65; H 7.2

The Splitting of Acetylene from 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V). The hydroxy ketone (V) (2g), toluene (10 ml), and powdered potassium hydroxide (0.05 g) were heated at 110° for 30 minutes. There was vigorous evolution of acetylene (detected by the Ilosvay reagent). The solution was cooled and washed with water; the solvent was driven off, and an attempt was made to distill the residue under reduced pressure. Only an insignificant amount of hexahydro-8a-methyl-1,6 (2H, 5H)-naphthalenedione (VIII) crystals, m.p. 60-62°, came over at 180°/2 mm. In admixture with a known sample there was no depression of melting point. The residue was an undistillable resin. Similar results were obtained when the hydroxy ketone was heated with sodium amyloxide.

Preparation of 1,2,3,4,4a,7,8,8a-Octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). A solution of the dienone (VII) (5.0 g) in ether (20 ml) was added at 5-10° over a period of ten minutes to a Grignard reagent prepared in the usual way from magnesium (3 g), methyl bromide (13 g), and absolute ether (100 ml). The solution was boiled for five minutes, cooled, and decomposed, firstly with ice, and then with 20% hydrochloric acid, until the flocs of magnesium hydroxide had disappeared. Careful extraction and distillation yielded 4.9 g (90%) of the dienol (XII) in the form of a thick, colorless liquid, b.p. 91-94°/0.5 mm, n_D^{20} 1.5260.

Found%: C 81.5; 81.3; H 11.05; 10.9

$C_{14}H_{22}O$. Calculated%: C 81.5; H 10.75

Preparation of 1,2,3,4,4a,5,6,8a-Octahydro-2,8a-dimethyl-8-vinyl-2-naphthol (XIIa). By a similar method, from 4 g of the dienone (VIIa), 3.8 g (87%) of the dienol (XIIa), b.p. 92-96°/0.5 mm and n_D^{20} 1.5235, was obtained.

Found %: C 81.5; H 11.0

$C_{14}H_{22}O$. Calculated %: C 81.5; H 10.75

Dehydration of 1,2,3,4,4a,7,8,8a-Octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). The dienol (XII) (4.9g), potassium hydrogen sulfate (2.5 g), and pyrogallol (0.05 g) were heated for 15 minutes under reduced pressure (45 mm) at 140° (at 150° towards the end). The usual treatment and fractionation yielded 2.9 g (66%) of 3,4,4a, 7, 8, 8a-hexahydro-6,8a-dimethyl-1-vinylnaphthalene (XVII) in the form of a colorless mobile liquid of pleasant odor, b.p. 70-72°/1 mm; n_D^{20} 1.5240; d_4^{20} 0.940; found MR_D 61.1; calculated MR_D 61.05.

Found %: C 89.0; 89.3; H 10.6; 10.4

$C_{14}H_{20}$. Calculated %: C 89.3; H 10.7

Dehydration of 1,2,3,4,4a,5,6,8a-Octahydro-2,8a-dimethyl-8-vinyl-2-naphthol (XIIa). The procedure was similar to that of the previous experiment. From 3.7 g of the dienol (XIIa), 2.0 g of 1,2,4a,5,6,8a-hexahydro-4a-7-dimethyl-4-vinylnaphthalene (XVIIa), b.p. 68-70°/0.5 mm and n_D^{20} 1.5220 was obtained.

Found %: C 88.6; H 10.7

$C_{14}H_{20}$ Calculated %: C 89.3; H 10.7

Condensation of the Dienol (XII) with Dimethyl Maleate. A mixture of the dienol (XII) (5.8 g) and dimethyl maleate (15 g; b.p. 84°/10 mm; n_D^{20} 1.4418) was heated at 100° for six hours. The excess of the ester was driven off under reduced pressure (1 mm) on a water bath (12.5 g). The residue was heated with finely ground potassium hydrogen sulfate (2.5 g) and pyrogallol (0.05 g) at 160-170° for 15 minutes under reduced pressure (25 mm). After the usual treatment, the product was vacuum-distilled.

Fraction I: b.p. 77-84°/1 mm; 1.2 g; n_D^{20} 1.5235.
Fraction II: b.p. 84-165°/1 mm; 0.2 g
Fraction III: b.p. 165-170°/1 mm; 4.3 g; n_D^{20} 1.5200
Residue: 1.5 g

Fraction III was the dicarboxylic ester XIV. It was a thick, odorless glycerol-like liquid.

Found %: C 72.9; H 8.5
$C_{28}H_{35}O_4$. Calculated %: C 72.3; H 8.5

Fraction III was dissolved in alcohol (10 ml), and 40% caustic soda (4 ml) was added. The solution was heated at 80-85° for three hours and then cooled. Water (10 ml) was added, the mixture was extracted with ether, and the aqueous layer was poured, under cooling, into 20% hydrochloric acid (10 ml). An oil separated, and this quickly solidified, giving a fine powder. Addition of 5 ml of ether accelerated this process. The crystals were filtered off under suction and washed several times with ether and with water. The product was the acid (XV) in the form of a white powder, which did not melt below 200°. A low carbon content was obtained in the analysis.

Condensation of the Dienol (XIIa) with Dimethyl Maleate. The procedure was similar to that in the previous experiment. From 3.7 g of the dienol (XIIa), 2.6 g of the ester (XIVa) was obtained. Hydrolysis yielded a viscous mass, which could not be caused to crystallize.

Dehydrogenation of the Acid (XV). A mixture of the acid (XV) (2.1 g), dry benzene (12 g), and 10% palladinized charcoal (1 g) was heated in an atmosphere of nitrogen in a rotating autoclave at 370° for 11 hours. Even then, the reaction was not complete, for after filtration, washing of the benzene solution with alkali, and removal of the solvent, only 0.4 g of a light-brown liquid remained. After one day, it had partially crystallized out. The crystals were filtered off and washed with a small amount of a mixture of petroleum ether and benzene (10:1). 2-Methylphenanthrene (XVI) (50 mg) was obtained in the form of fine, white crystals, m.p. 57-58.5°.

Found %: C 93.4; H 6.35
$C_{15}H_{12}$. Calculated %: C 93.7; H 6.3

The picrate formed (from methanol) light-brown needles, m.p. 115-117°. Dehydrogenation of the acid (XVa), which was isolated in an impure form (viscous mass), did not give clear results: it was not found possible to isolate a crystalline hydrocarbon.

Condensation of 3,4,4a,7,8,8a-Hexahydro-6-8a-dimethyl-1-vinylnaphthalene (XVII) with 2-Cyclohexen-1-one. The triene (XVII) (1.2 g) and freshly distilled 2-cyclohexen-1-one (3.1 g; b.p. 63°/22 mm; n_D^{20} 1.4870) were heated in a sealed tube in an atmosphere of carbon dioxide at 200° for four hours. Fractionation gave the following fractions:

Fraction I: b.p. 50-60°/10 mm; 1.6 g
Fraction II: b.p. 40-150°/1 mm; 1.0 g
Fraction III: b.p. 150-155°/1 mm; 0.5 g
Residue: 0.7 g

Fraction III consisted mainly of the ketone (XVIII) contaminated with self-condensation products of cyclohexenone (this is shown by the low carbon content). It was used in further reactions without purification.

Condensation of 1,2,4a,5,6,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XVIIa) with 2-Cyclohexen-1-one. The procedure was similar to that in the preceding experiment. From 2.2 g of the triene, 1.2 g of crude ketone (XVIIIa) b.p. 145-155°/1 mm, was obtained. It was used in further reactions without purification.

Kizhner Reduction of the Ketone (XVIII), and Dehydrogenation of the Hydrocarbon Formed (XIX). Crude ketone (XVIII) (0.5 g) was mixed with diethylene glycol (3 ml), hydrazine hydrate (0.4 ml) was added, and the mixture was heated for five minutes. The mixture was transferred to a Favorsky flask provided with ground joints, a solution of sodium (0.4 g) in diethylene glycol (10 ml) was added, and the turbid solution was heated in a feeble stream of nitrogen for 10 hours at 200-205° and for 3 hours at 220°. In the course of this treatment a small amount of distillate came off. The reaction mixture was diluted with twice its volume of water, and the solution obtained was extracted with ether. The ether extract was washed twice, with 10% hydrochloric acid and with water. The ether solution was dried with magnesium sulfate, the ether was driven off, and the residue was evaporated under reduced pressure on a water bath, yielding 0.4 g of a thick light-brown liquid, which was impure hydrocarbon XIX. Without being purified, it was hydrogenated as follows.

The hydrocarbon (XIX) was dissolved in 14 ml of benzene, 0.3 g of 10% palladinized charcoal was added, and the mixture was heated in an atmosphere of nitrogen in a rotating autoclave at 350° for six hours. The mixture was filtered, benzene was removed under reduced pressure, and a residue was obtained that partially crystallized out. The crystals were filtered off under suction and were washed four times with petroleum ether. The product was 14 mg of 2-methylchrysene in the form of white plates, m.p. 222-223°. The picrate formed light-orange needles, m.p. 145.5-146°.

Found %: C 94.45; 94.1; H 6.0; 6.1

$C_{19}H_{14}$. **Calculated %:** C 94.2; H 5.8

Kizhner Reduction of the Ketone (XVIIIa) and Dehydrogenation of the Hydrocarbon Formed (XIXa). The procedure was similar to that in the preceding experiment, but crude hydrocarbon (XIXa) distilled over. From 1.2 g of crude ketone (VIIIa), 0.45 g of hydrocarbon (XIXa), b.p. 126-130°/0.5 mm, was obtained; it was dissolved in 10 ml of benzene, 0.3 g of palladium on charcoal (10% Pd) was added, and the mixture was heated in an atmosphere of nitrogen in a rotating autoclave for 3 hours at 320° and 3.5 hours at 350°. The solution was filtered, the benzene was driven off, and the residue was dissolved in 2 ml of petroleum ether and cooled to −15°. Crystals were precipitated, and after two hours these were filtered off under suction and washed with cold petroleum ether. The product was 15 mg of 3-methylchrysene, m.p. 166-169°. The picrate formed orange needles, m.p. 160-161°.

SUMMARY

1. A detailed investigation has been made of the conditions for the condensation of 2-methyl-2-cyclohexen-1-one (II) with 2-methoxy-1,3-butadiene (I).

2. It has been shown that this condensation proceeds in two directions with formation of 2,3,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III) and 2,3,4a,5,8,8a-hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalenone (IIIa) in a ratio of approximately 5:1 The yield of condensation products has been increased from 25 to 45-50%.

3. A detailed study has been made of the condensation of the compounds III and IIIa with alkali-metal acetylides in liquid ammonia. By this means yields of 50-55% of the acetylenic hydroxy ketones (V) and (Va) have been obtained, and these have been hydrogenated selectively in the presence of a Pd catalyst, yielding the vinyl hydroxy ketones (VI) and (VIa), which have been dehydrated with potassium hydrogen sulfate to give the dienones (VII) and (VIIa). The structures of these dienones and related compounds have been rigorously proved by converting them into known methylchrysenes (XX and XXa), and also by converting the dienone (VII) into the known 2-methylphenanthrene.

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CATALYTIC AMINATION OF KETONES OF VARIOUS STRUCTURES

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In a previous investigation [1] we have shown that reductive amination of acetone and cyclohexanone in presence of platinized silica gel gives the corresponding primary amines in good yield. This fact prompted us to continue the investigation for other ketones in order to determine the effect of the number of carbon atoms in ketone molecules, having like or unlike radicals, on the yield of amine in the reductive amination reaction. In the present investigation we have investigated the reductive amination of 3-pentanone, 4-heptanone, 2-butanone, 2-octanone, and cyclopentanone in presence of platinized silica gel.

EXPERIMENTAL

Ketone vapor, together with excess of ammonia and hydrogen, was passed through a quartz tube containing 80 ml of platinized silica gel, which was mounted in an electric furnace fitted with a thermoregulator. The reaction products passed to a receiver cooled with snow and salt. The duration of each experiment was 30 minutes. The properties of the ketones investigated are given in Table 1.

TABLE 1

Properties of Investigated Ketones

Ketone	Our preparation				Data in literature			References
	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	B.p. (°C, corr.)	Specific gravity	Refractive index	
3-Pentanone	101	758	0.8149	1.3921	101.08	$d_4^{19.1}$ 0.8159	$n_D^{19.1}$ 1.39265	[2 and 3]
4-Heptanone	143	759	0.8203	1.4064	143.52	$d_4^{21.7}$ 0.8160	n_D^{21} 1.4047	[2 and 3]
2-Butanone	77-78	756	0.8087	1.3774	78.6	d_4^{20} 0.8054	$n_D^{15.9}$ 1.3807	[4 and 5]
2-Octanone	171	752	0.8193	1.4158	172.92	d_4^{20} 0.8185	n_D^{20} 1.41613	[2 and 6]
Cyclopentanone	128-129	748	0.9484	1.4363	129	d_4^{20} 0.9480	n_D^{20} 1.4366	[7]

The condensates obtained were dried with solid caustic potash, and the total contents of amine nitrogen were determined by Francois' method [8]

Information on experimental conditions and the results of the reductive amination of the above ketones are given in Table 2, on page 82.

Experiment No. 18, on the amination of 2-butanone at 200°, was carried out for 4 hours 30 min, in order to find out how long the catalyst continued to function. Separate portions of condensate were collected every 30 minutes, and analyses for amine-nitrogen content were carried out for the 1st, 3rd, 5th, 7th, and 9th portions. Experiments having the same purpose were carried out also with 2-octanone at 200°. One of these (No. 19) was performed with fresh catalyst, and another (No. 24) with previously used, nonregenerated catalyst.

The experiments showed that in the amination of cyclopentanone the catalyst was very quickly covered with resin, so that the pieces became stuck together. In this case, therefore, the catalyst was ether-extracted after each experiment to remove the greater part of the resin, and was then regenerated by roasting and blowing with air.

The condensates from the amination experiments on 2-butanone, 3-pentanone, and 4-heptanone, which contained considerable amounts of amine nitrogen, were investigated for the isolation of their components and their characterization. For this purpose, the condensate was acidified with dilute hydrochloric acid, which caused the liquid to separate into two layers. The upper layer contained unchanged ketone, and the lower layer contained amines, in the form of their water-soluble hydrochlorides, in admixture with a little ketone, which was distilled off and added to the ketone layer. The unchanged ketone was dried and distilled. The aqueous solution of amine hydrochlorides was evaporated down to low volume, and excess of solid caustic alkali was added. The amine that separated was dried with caustic potash and distilled.

TABLE 2

Reductive Amination of Ketones

Expt. No.	Temp. (°C)	Amt. taken for reaction			Amt. of condensate(g)		Amine-nitrogen content(%)	Amine content of condensate (%)
		Ketone (g)	Ammonia (g)	Hydrogen (liters)	Crude	After drying		
				3-Pentanone				
1	140	6.5	3.7	3.8	6.0	5.9	4.53	28.1
2	170	6.5	3.7	3.8	6.5	6.2	5.31	32.9
3	200	6.5	3.7	3.8	7.9	7.7	4.34	26.9
4	230	6.5	3.7	3.8	7.2	6.5	4.10	25.4
5	260	6.5	3.7	3.8	7.3	6.1	5.49	34.0
6	290	6.5	3.7	3.8	7.8	6.1	3.22	20.0
				4-Heptanone				
7	170	6.6	3.0	3.7	5.0	4.9	3.76	30.8
8	200	6.6	3.0	3.7	5.8	5.7	5.05	41.4
9	230	6.6	3.0	3.7	6.9	6.8	4.11	33.7
10	260	6.6	3.0	3.7	7.4	6.5	2.96	24.3
				2-Butanone				
11	150	6.4	4.5	3.5	6.2	4.2	2.47	12.8
12	170	6.4	4.2	3.5	6.6	6.0	3.38	17.6
13	200	6.4	4.3	3.5	6.5	6.0	4.19	21.7
14	230	6.4	4.5	3.5	6.7	6.2	3.85	20.0
15	260	6.4	4.5	3.5	6.6	6.0	2.98	15.5
16	290	6.4	4.5	3.5	6.6	5.8	2 87	14.9
17	320	6.4	4.5	3.5	6.7	5.9	2.79	14.5
18-1	200	6.4	4.5	3.5	6.2	5.8	4.40	22.9
18-3	200	6.5	4.5	3.5	6.5	6.0	4.29	22.3
18-5	200	6.5	4.5	3.5	6.5	6.0	3.79	19.7
18-7	200	6.5	4.5	3.5	6.5	6.1	3.29	17.1
18-9	200	6.5	4.5	3.5	6.4	6.0	3.28	17.1
				2-Octanone				
19	200	6.6	2.0	2.5	6.6	6.0	1.83	16.8
20	230	6.6	2.0	2.5	6.6	6.1	1.73	16.1
21	260	6.6	2.0	2.5	8.1	7.0	1.56	14.3
22	290	6.6	2.0	2.5	8.1	7.0	1.17	10.8
23	320	6.6	2.0	2.5	7.3	6.2	1.16	10.7
24	200	6.6	2.0	2.5	6.0	5.5	0.96	8.8
				Cyclopentanone				
25	150	7.6	4.2	3.2	3.0	1.0	1.63	9.9
26	170	7.6	4.2	3.2	3.8	1.2	1.85	11.3
27	200	7.6	4.2	3.2	4.5	2.3	1.29	7.9
28	230	8.1	4.5	3.2	3.4	1.7	1.62	9.9
29	260	7.9	4.2	3.2	5.0	3.4	1.41	8.6
30	290	7.9	4.5	3.2	6.1	4.0	0.70	4.3
31	320	7.6	4.2	3.2	8.2	6.1	0.42	2.6

From 22.0 g of united condensate obtained from the reductive amination of 3-pentanone and containing 4.51% of amine nitrogen, 13.0 g of unchanged ketone and 4.7 g of amine were isolated. The isolated ketone had b.p. 100°/758 mm, d_4^{20} 0.8148, and n_D^{20} 1.3922; it had remained, therefore, fairly pure. The amine had b.p. 86°/746 mm, d_4^{20} 0.7479 and n_D^{20} 1.4063. Analysis gave:

Found %: C 68.90; H 15.09; N 16.27
$C_5H_{13}N$. Calculated %: C 68.89; H 15.04; N 16.07

The amine obtained, therefore, was close in properties and composition to 1-ethylpropylamine, for which the literature gives b.p. 90-91° and $d^{22.5}$ 0.7478 [9].

From 15.2 g of condensate from the reductive amination of 4-heptanone (amine-nitrogen content 4.15%), 8.0 g of unchanged ketone and 4.5 g of amine were isolated. The isolated ketone had b.p. 143°/758 mm, d_4^{20} 0.8205 and n_D^{20} 1.4062; these properties correspond to the original 4-heptanone. The amine obtained boiled over the range 138-140°/760 mm and had d_4^{20} 0.7657 and n_D^{20} 1.4178.

Found %: C 72.98; H 14.59; N 12.18
$C_7H_{17}N$. Calculated %: C 72.95; H 14.89; N 12.16

In its properties and analysis the amine obtained corresponded to 1-propylbutylamine, for which the literature [10] gives: b.p. 140-141°/745 mm and d_4^{24} 0.7671.

From 52.1 g of united condensate containing 3.56% of amine nitrogen, which was obtained by reductive amination of 2-butanone, 31.5 g of unchanged ketone and 8 g of amine were isolated. The ketone had b.p. 77-79°/746, d_4^{20} 0.8084 and n_D^{20} 1.3766, which correspond to the original 2-butanone. The amine obtained had b. p. 61-63°/750 mm, d_4^{20} 0.7155 and n_D^{20} 1.3948.

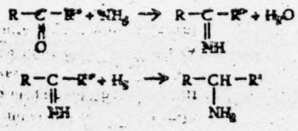
Found %: C 65.56; H 15.19; N 19.08
$C_4H_{11}N$. Calculated %: C 65.67; H 15.17; N 19.16

In its properties and analysis the synthesized amine was very close to 1-methylpropylamine, which, according to the literature, has b.p. 63°/760 mm [11]; d^{22} 0.718 [9] and $n_D^{17.7}$ 1.3950 [12].

The yields of these three amines, based on the amounts of ketone that reacted, were: 1-ethylpropylamine, 51.6%; 1-propylbutylamine, 64.2%; and 1-methylpropylamine, 46.3%. It may be noted, for comparison, that in the reductive amination of acetone [1] at 240°, the condensate contained 9% of amine nitrogen, which corresponds to a 38% content of isopropylamine, and in the experiments with cyclohexanone [1], the condensate contained 12.7% of amine nitrogen, or 89.6% of cyclohexylamine.

DISCUSSION OF RESULTS

The experiments show that, over a wide range of temperatures (140-320°), reductive amination of ketones over platinized silica gel leads to the formation of the corresponding primary amines. The reactions occurring may be expressed as follows:



$$R-\underset{\underset{O}{\|}}{C}-R' + NH_3 \rightarrow R-\underset{\underset{NH}{\|}}{C}-R' + H_2O$$

$$R-\underset{\underset{NH}{\|}}{C}-R' + H_2 \rightarrow R-\underset{\underset{NH_2}{|}}{CH}-R'$$

The optimum temperature for the reaction lies in the range 170-240°; it is about 240° for acetone, about 200° for 2-butanone and 4-heptanone, and about 170° for 3-pentanone. Rise in temperature above 240° leads to a reduction in the amount of condensate and to the formation of resinous products, which cause a rapid fall in the activity of the catalyst. As regards the working life of the catalyst, the experiments on the reductive amination of acetone and 2-butanone show that platinized silica gel does not lose its activity for at least 4 hr. 30 min. and that it can be readily regenerated by heating in a stream of air.

The structure of the ketone and the length of its carbon chain have a considerable effect on the yield of amine. The ketones investigated may be divided into three groups: aliphatic ketones having like radicals, aliphatic ketones having unlike radicals, and ketones of the alicyclic series. Ketones of the first group (acetone, 3-pentanone, 4-heptanone) are readily aminated and give the highest yields of the corresponding amines. In the experiments with these ketones, condensates having amine contents of 34-41.4% were obtained.

Ketones of the second group (2-butanone, 2-octanone) give lower yields of amines than ketones of the first group, condensates having amine contents of 16.1-21.7% being obtained. The experiments with 2-octanone indicate that an appreciable increase in the number of carbon atoms in one of the radicals of the ketone, in comparison with the other, results in an appreciable reduction in the yield of amine.

As regards alicyclic ketones, the experiments show that in this series the yield of amine depends on the stability of the ketone under the given conditions. Cyclohexanone, which does not resinify under the conditions of reductive amination, gives a high yield of cyclohexylamine. Cyclopentanone, which readily undergoes autocondensation under the amination conditions, gives catalyzates having a low (not above 11.3%) content of cyclopentylamine.

SUMMARY

1. Reductive amination of ketones in presence of platinized silica gel gives only primary amines.

2. The optimum reaction temperature lies in the range 170-240°.

3. Aliphatic ketones having like radicals give higher yields of amines than ketones having unlike radicals.

4. Equal increases in the numbers of carbon atoms of the two identical radicals of a ketone do not lead to reduction in yield of amine.

5. Increase in the number of carbon atoms in only one of the radicals of the ketone leads to a reduction in the yield of amine. This reduction in yield is the greater, the greater the difference in the numbers of carbon atoms in the two radicals of the ketone.

6. In the reductive amination reaction, cyclopentanone gives insignificant yields of amine, owing to the occurrence under these conditions of condensation and resinification reactions.

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HYDROGENATING AND DEHYDROGENATING POWER OF NICKEL CATALYSTS ON VARIOUS CARRIERS

N. I. Shuikin, Kh. M. Minachev, and L. M. Feofanova

Thanks to the work of Zelinsky and coworkers, nickel catalysts on various carriers (aluminum oxide, silica gel, activated charcoal) have received wide application in the practice of hydrogenation and dehydrogenation catalysis. It should be noted, however, that nickel catalysts on carriers have generally been prepared with a relatively high nickel content — up to 50% [1]. At such a high nickel content, hydrocarbons undergo considerable breakdown under dehydrogenation conditions at 300° and above. Thus, one of us [2] has shown that when methylcyclohexane is passed at 330° over a Ni/Al_2O_3 catalyst containing 50% of nickel, the gas leaving consists of 57.1% of hydrogen and 42.1% of methane; at 400°, cyclohexane is broken down completely to methane and hydrogen.

Gaverdovskaya [3] has observed that, already at 300°, a nickel catalyst (47% of nickel on silica gel), causes the breakdown of about 20% of cyclohexane. Also, it should be noted that nickel catalysts of high nickel content (of the order of 50%) lose their activity much more rapidly than catalysts of lower active nickel content.

It was shown in one of our investigations [4] that nickel catalysts prepared by impregnation of active charcoal with nickel nitrate solution and containing from 4 to 0.5% nickel are very efficient for the hydrogenation of the benzene ring. Their activity for dehydrogenation reactions, however, is much below the optimum, and this method of preparation permits us to obtain highly active catalysts only for hydrogenation purposes. In this investigation we decided to study the hydrogenating and dehydrogenating powers of nickel catalysts containing from 12 to 20% of nickel on various carriers.

Apart from the paper of Gaverdovskaya [3] already mentioned, there are practically no data in the literature on the activity and stability of nickel catalysts prepared on various carriers. Gaverdovskaya attempted to determine the influence of the carrier on the activity of a nickel catalyst. With this objective, a series of catalysts was prepared: they consisted of nickel precipitated on Al_2O_3, SiO_2, asbestos, active charcoal, Cr_2O_3, and ZnO. The most active for the dehydrogenation of the cyclohexane ring were the first two catalysts, and the least active were nickel on ZnO and nickel on Active charcoal. The author was not successful in establishing the relation of the dehydrogenating power of a nickel catalyst to the chemical nature of the carrier, for different methods were used for the preparation of the various catalysts. Also, the catalysts prepared and investigated by Gaverdovskaya varied greatly in nickel content (from 4.3 to 47.1%).

Our investigation of the properties of nickel catalysts precipitated on Al_2O_3, ZnO, Cr_2O_3, MgO, and Fe_2O_3 has shown that the highest dehydrogenating activity is exhibited by nickel on Al_2O_3 and on ZnO, and the lowest activity by nickel precipitated on ferric oxide. Catalysts containing 11-19% of nickel precipitated on Al_2O_3 or ZnO dehydrogenate cyclohexane to the extent of 80-90% at 300°; under the same conditions, nickel on ferric oxide dehydrogenates cyclohexane only to the extent of 10%. The degree of conversion of cyclohexane over the same catalyst at 400° was 80%. All the catalysts studied, with the exception of Ni on Fe_2O_3, have high hydrogenating power and preserve it for a long time.

In the reduction of the catalysts a very interesting phenomenon was observed. Under identical conditions of reduction with hydrogen (temperature, time, amount of hydrogen), nickelous oxide was most readily reduced to nickel in the catalysts NiO/ZnO and NiO/Fe_2O_3; it was most difficult to reduce when in admixture with MgO. This fact is evidently to be explained by the formation of stable compounds of difficultly reducible nickelous oxide with the metal oxides applied as carriers. A similar fact was observed by Hill and Selwood [5], who were unable to reduce NiO/MgO and NiO/TiO_2 to Ni/MgO and Ni/TiO_2. They attributed their lack of success to the tendency of nickel ions to build themselves into the lattice of the carrier.

It follows from this short review and from the results of our experiments that to obtain active, stable nickel catalysts, they must be prepared with a relatively low nickel content (15-20%) and ZnO or Al_2O_3 must be used as carrier.

EXPERIMENTAL

Preparation of Catalysts. All the catalysts studied were prepared by the coprecipitation of molar solutions of the nitrates of the corresponding metals with a 30% solution of caustic soda. The hydroxides formed were washed with pure tap water to free from NO_3^- ions, filtered off, dried at 120-130°, ground to a powder, and converted into tablets of cylindrical form (diameter, 3-4 mm; length, 5-6 mm) in a special press.

Experimental Procedure. The experiments on the hydrogenation and dehydrogenation of hydrocarbons were carried out in the usual continuous-flow apparatus, as previously described [6]. In all of the experiments the volume of reduced catalyst was 50 ml. The reduction of the catalyst was carried out in a stream of electrolytic hydrogen with gradual elevation of the temperature to 350-360°. In the reduction process, readings were made of the time and amount of hydrogen used. The nickel contents of the catalysts were determined by dissolving the catalyst in nitric acid, neutralizing the solution with ammonia until slightly alkaline, and precipitating with dimethylglyoxime.

The rate of passing cyclohexane vapor was 0.3 liter per liter of catalyst per hour; the rate for benzene was 0.06 liter per liter of catalyst per hour. Analysis of the issuing gas was performed in an Orsat–Lunge apparatus. The degree of conversion of cyclohexane into benzene, and of benzene into cyclohexane, was determined refractometrically [7].

Properties of Starting Materials. The cyclohexane used in the experiments had the following constants: b.p. 80°/760 mm, n_D^{20} 1.4264 and d_4^{20} 0.7780. The benzene (thiophene-free) had b.p. 80.0°/754 mm, n_D^{20} 1.5005 and d_4^{20} 0.8782.

Activity and Stability of the Nickel Catalysts Studied in Hydrogenation and Dehydrogenation Reactions. The initial dehydrogenation and hydrogenation activities of the catalysts investigated are given in Table 1. It will be seen from the results given in this table that nickel catalysts precipitated on Al_2O_3 and on ZnO have high dehydrogenating power. Catalysts precipitated on Cr_2O_3 and on MgO are of lower activity; and nickel on Fe_2O_3 is practically worthless as a dehydrogenation catalyst. All the samples studied, with the exception of Ni/Fe_2O_3, completely hydrogenate benzene to cyclohexane in one passage at 160-170°.

TABLE 1

Initial Hydrogenation and Dehydrogenation Activities of Nickel Catalysts on Various Carriers

Catalyst No.	Composition of catalyst	Cyclohexane		Benzene	
		n_D^{20} of catalyzate	% conversion	n_D^{20} of catalyzate	% conversion
1	14.4 Ni + 85.6 Al_2O_3	1.4758	74	1.4265	100
2	11.3 Ni + 88.7 ZnO	1.4790	78	1.4265	100
3	12.6 Ni + 87.4 Cr_2O_3	1.4570	51	1.4320	89.2
4	16.2 Ni + 83.8 MgO	1.4530	45	1.4265	100
5	16.9 Ni + 83.1 Fe_2O_3	1.4320	11	1.4950	5.5
6	19.5 Ni + 80.5 Al_2O_3	1.4870	87	1.4264	100
7	18.1 Ni + 81.9 ZnO	1.4830	82	1.4268	100
8	17.0 Ni + 83.0 Cr_2O_3	1.4725	70	1.4265	100
9	22.0 Ni + 78.0 MgO	1.4670	63	1.4260	100
10	21.1 Ni + 78.9 Fe_2O_3	1.4352	18	1.4948	5.8

With the object of determining the stabilities of the catalysts after functioning for a long period following the measurement of their initial activities, cyclohexane was passed, and then benzene, under the given conditions. The variation in hydrogenation and dehydrogenation properties of the catalysts studied are given in Figures 1, 2a and 2b. As will be seen from Fig. 1, the hydrogenating power of an Ni/Al_2O_3 catalyst remained quite unchanged after 80 hours. During the same period, the activities of Ni/ZnO and Ni/Cr_2O_3 catalysts fell by 18 and 20% respectively. The degree of dehydrogenation of cyclohexane fell gradually with time. The relatively high stabilities of the catalysts we have studied in hydrogenation and dehydrogenation reactions are evidently to be explained by the comparatively low concentration of finely dispersed nickel on the highly developed surface of the carriers. In this case the active nickel is distributed on the carrier in such a way that its splitting power is considerably weakened in comparison with that of the highly concentrated forms of nickel catalysts described in the investigations cited [1,3].

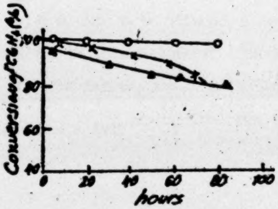

Fig. 1. Variation of hydrogenation properties of catalysts with time;
o – 19.5% Ni + 80.5% Al_2O_3;
x – 18.1% Ni + 81.9% ZnO;
Δ – 17.0% Ni + 83.0% Cr_2O_3.

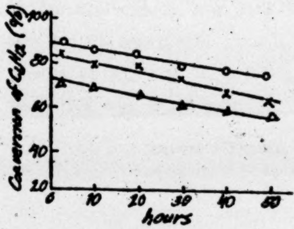

Fig. 2 A. Variation of dehydrogenation properties of catalysts with time:
o – 19.5% Ni + 80.5% Al_2O_3;
x – 18.1% Ni + 81.9% ZnO;
Δ – 17.0% Ni + 83.0% Cr_2O_3.

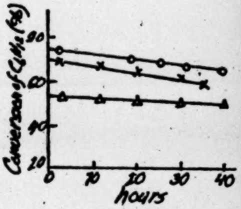

Fig. 2B. Variation of dehydrogenation properties of catalysts with time:
o – 14.4% Ni + 85.6% Al_2O_3;
x – 11.3% Ni + 85.6% ZnO;
Δ – 12.6% Ni + 87.4% Cr_2O_3.

Specially designed experiments showed that, right up to 350°, the catalyst that we have studied did not cause methane breakdown of cyclohexane; only above 350° did the splitting effect of these catalysts become appreciable. The experimental results obtained are given in Table 2. As will be seen from these results, only at 370° and higher do the catalysts studied have appreciable splitting action on hydrocarbons. The amounts of saturated hydrocarbons formed indicate that the carrier also has a definite effect on the extent of the decomposition of cyclohexane.

TABLE 2

Effect of Temperature on the Breakdown of Cyclohexane in Presence of Nickel Catalysts on Various Carriers

Temperature of Expt. (°C)	Composition of catalyst (%)					
	19.5% Ni + 80.5% Al_2O_3		18.1% Ni + 81.9% ZnO		17.0% Ni + 83.0% Cr_2O_3	
	H_2 (%)	Saturated hydrocarbons (%)	H_2 (%)	Saturated hydrocarbons (%)	H_2 (%)	Saturated hydrocarbons (%)
300	100	0	100	0	100	0
325	100	0	100	0	100	0
350	100	0	100	0	100	0
375	89	11	85.1	14.9	81.1	18.9
400	–	–	–	–	78	22.0

SUMMARY

1. A study has been made of the dependence of the hydrogenating and dehydrogenating powers of a number of nickel catalysts on their contents of finely dispersed nickel and on the nature of the carriers.

2. It has been shown that the most active nickel catalysts are obtained when Al_2O_3, ZnO, or Cr_2O_3 is used as carrier; nickel on ferric oxide is of no value as a hydrogenation or dehydrogenation catalyst.

3. It has been established that catalysts on carriers having a nickel content of up to 20% do not split cyclohexane at temperatures below 350°.

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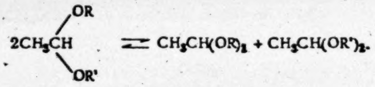
REACTIONS OF VINYL ETHERS

COMMUNICATION VIII. REACTIONS OF ACETALS DERIVED FROM ETHYLENE GLYCOL

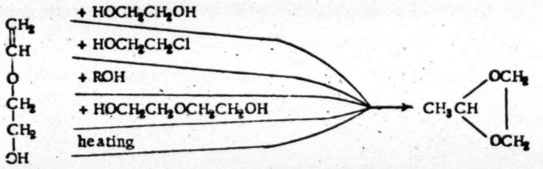
M. F. Shostakovsky, N. A. Gershtein, and Z. S. Volkova

It has already been noted in previous papers [1-3] that mixed acetals of the type $CH_3CH\begin{smallmatrix}OR\\ OR'\end{smallmatrix}$ undergo partial disproportionation when distilled:

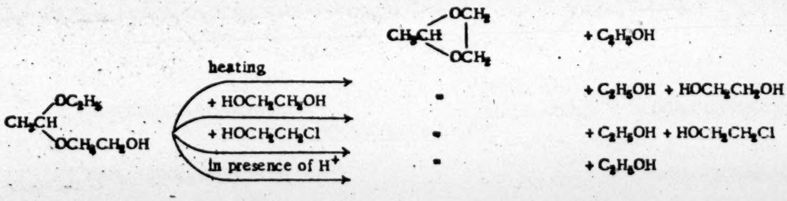


$$2CH_3CH\begin{smallmatrix}OR\\ OR'\end{smallmatrix} \rightleftharpoons CH_3CH(OR)_2 + CH_3CH(OR')_2.$$

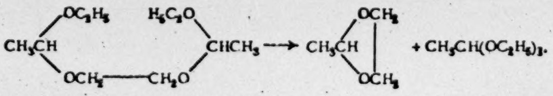
Acetals of ethylene glycol are particularly susceptible to such changes. Attempts to prepare hydroxy acetals by direct addition of alcohols to 2-vinyloxyethanol were not successful owing to the rapidity with which the vinyl ether undergoes cyclization, when heated, or in presence of acid catalyst.


CH_2
CH
O
CH_2
CH_2
OH
$+ HOCH_2CH_2OH$
$+ HOCH_2CH_2Cl$
$+ ROH$
$+ HOCH_2CH_2OCH_2CH_2OH$
heating
CH_3CH
OCH_2
OCH_2

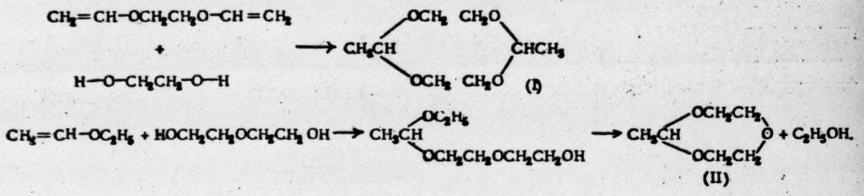
Moreover, acetaldehyde ethyl 2-hydroxyethyl acetal, prepared by a different method [4], is also notable for its high instability, and shows a great tendency to react with formation of the same ethylene cyclic acetal (2-methyl-1,3-dioxolane):


CH_3CH
OC_2H_5
OCH_2CH_2OH
heating
$+ HOCH_2CH_2OH$
$+ HOCH_2CH_2Cl$
in presence of H^+
CH_3CH
OCH_2
OCH_2
$+ C_2H_5OH$
$+ C_2H_5OH + HOCH_2CH_2OH$
$+ C_2H_5OH + HOCH_2CH_2Cl$
$+ C_2H_5OH$

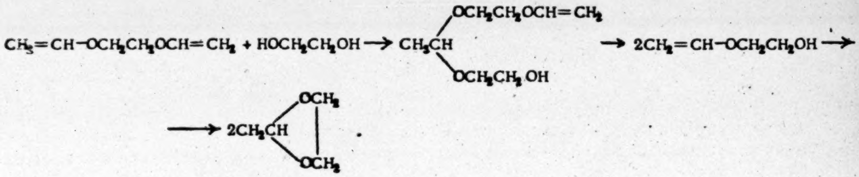
Even the diethyl ethylene diacetal (1,2-di(1-ethoxyethoxy)ethane), which has no free hydroxyl group, splits on being distilled at atmospheric pressure with formation of 2-methyl-1,3-dioxolane:


CH_3CH
OC_2H_5
OCH_2
H_5C_2O
$CHCH_3$
CH_2O
CH_3CH
OCH_2
OCH_2
$+ CH_3CH(OC_2H_5)_2.$

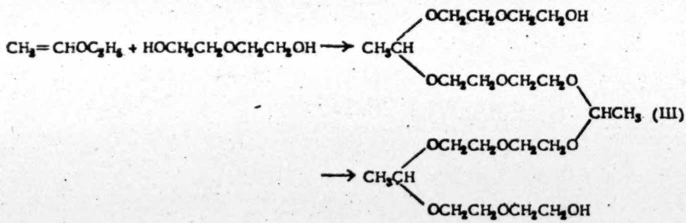
We have observed similar reactions when attempting to effect the synthesis of the cyclic diacetal (I) from ethylene glycol and the heterocyclic acetal (II) from diethylene glycol, in accordance with the following equations:



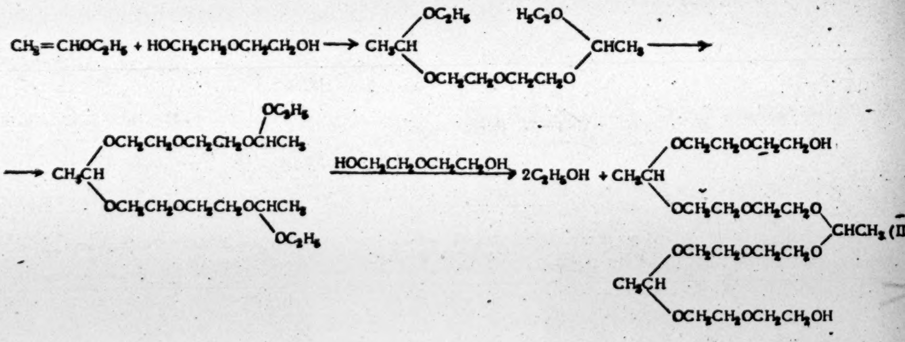
However, in the first case, instead of the expected cyclic diacetal (I), the same 2-methyl-1,3-dioxolane was isolated in quantitative yield. The result obtained is to be explained by the decomposition, under the conditions of the reaction, of the 2-hydroxyethyl 2-vinyloxyethyl acetal formed, giving two molecules of 2-vinyloxyethanol, which then undergoes cyclization:



Similarly, in the second case (synthesis of the heterocyclic acetal (II)), we obtained completely unexpected results, a 90% yield of a dihydroxy polyacetal derived from diethylene glycol being obtained:



It is evident that here we have again encountered a series of readily occurring reactions, which, we think, may be schematically represented as follows:



It is relevant here to point out that symmetrical acetals also readily undergo various reactions similar to those of compounds having multiple bonds [5-10]. The reactivity of acetals is related to their property of readily breaking down with formation of vinyl ethers as intermediate compounds; we have previously drawn attention to this fact [1, 2, 11]. We shall not consider the mechanism of these reactions in detail here, since we shall publish a special communication on this question.

EXPERIMENTAL

1. Reaction of 2-Vinyloxyethanol with Ethylene Glycol

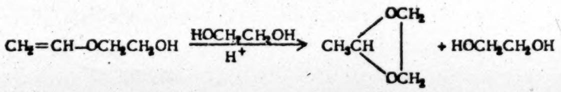
The reaction was carried out in a three-necked flask fitted with reflux condenser, mercury-sealed mechanical stirrer, thermometer, and dropping funnel. Ethylene glycol (28 g, i.e. 0.45 mole), containing one drop of 33% hydrochloric acid, was added to chemically pure 2-vinyloxyethanol (b.p. 139.9°, n_D^{20} 1.4360; 39.0 g, i.e. 0.44 mole). Addition of the first drops of ethylene glycol was accompanied by an immediate rise in temperature from that of the room to 100°. Addition of ethylene glycol was discontinued until the reaction mixture had been cooled to 30°, when the remaining ethylene glycol was added; this further addition of ethylene glycol and catalyst did not, however, result in a further exothermic effect. The reaction mixture was set aside overnight and then fractionally distilled in a stream of nitrogen, yielding:

Fraction I, b.p. 65-68° at 758 mm; 2.8 g
Fraction II, b.p. 82.3-84° at 758 mm; 32.8 g
Fraction III, b.p. 84-186° at 758 mm; 2.3 g
Fraction IV, b.p. 74-75° at 3 mm; 26.4 g.

Fraction II, after treatment with sodium, yielded 31.9 g (82%) of the cyclic acetal 2-methyl-1,3-dioxolane, b.p. 82.6-82.9° at 762 mm; n_D^{20} 1.3981; d_D^{20} 0.9822; found MR_D 21.42; calculated for $C_4H_8O_2$ MR_D 21.758. The literature [12] gives b.p. 82.5; d^0 1.002.

Hydrolysis with 2% sulfuric acid and estimation of the acetaldehyde formed with sodium bisulfite indicated a $C_4H_8O_2$ content of 98.53% and 100.1% of that required theoretically. Fraction (IV) was found to be ethylene glycol: b.p. 196-197° at 760 mm, n_D^{20} 1.4320; yield 94%.

Under these reaction conditions 2-vinyloxyethanol isomerizes:

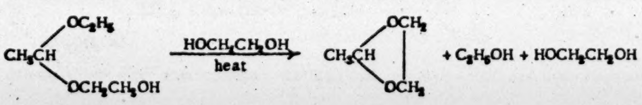


2. Reaction of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal with Ethylene Glycol

An equimolecular mixture of 34 g of the ethyl 2-hydroxy acetal (b.p. 59.2°/2.5 mm, n_D^{20} 1.4180; d_4^{20} 0.9753) and 16 g of ethylene glycol (b.p. 196-197°, n_D^{20} 1.4320) was heated in a rotating stainless-steel 500 ml autoclave for 10.5 hours at 200-220°. The pressure in the autoclave attained 12-14 atm. The product (43.07 g) was a homogeneous, light-yellow, mobile liquid, from which two fractions were isolated;

Fraction I, b.p. 73-74°, 23.9 g; $n_D^{28.8}$ 1.3829.
Fraction II, b.p. 123-123.2° at 50 mm; 16.11 g; $n_D^{28.8}$ 1.4318

Fraction (I) was a mixture of the cyclic acetal and ethanol. It was not found possible to resolve this mixture with the aid of a column of 40 theoretical plates and a reflux index of 7, and the whole mass came over at 72.6-73.2° and had n_D^{18} 1.3830. By treating this fraction with sodium we succeeded in obtaining 2-methyl-1,3-dioxolane having the following constants: b.p. 82.7-83°; n_D^{20} 1.3982. Fraction (II) was unchanged ethylene glycol. It appears, therefore, that acetaldehyde ethyl 2-hydroxyethyl acetal reacts similarly to 2-vinyloxyethanol:

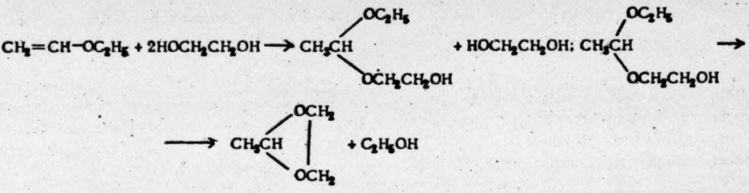


3. Reaction between Ethyl Vinyl Ether and Ethylene Glycol in the Molar Ratio of 1:2

The reaction was carried out in an autoclave (150-180°, 8-10 atm, 12 hr, 30 min). Ethylene glycol (124 g, i.e. 2 moles) and ethyl vinyl ether (70 g, i.e. 1 mole) yielded a liquid (189.1 g), which gave on fractionation:

Fraction I, b.p. 52-75° (mainly 74-75°; 100.55 g; $n_D^{22.8}$ 1.3820
Fraction II, b.p. 113-115° at 31 mm; 67.75 g; n_D^{23} 1.4310
Trapped in coil at −14-15° 12.70 g; n_D^{23} 1.3830

Fraction (I) and the contents of the coil were treated together several times with sodium, yielding 60.2 g (70 %) of 2-methyl-1,3-dioxolane, b.p. 82.5-83.2°, n_D^{20} 1.3982. Fraction (II) corresponded to ethylene glycol (54% of original), b.p. 195-196°, n_D^{20} 1.4320. The result of the reaction can be expressed by the following scheme:

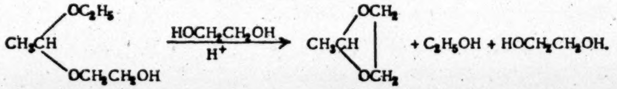


4. Reaction of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal with Ethylene Glycol in Presence of Catalysts

The conditions were the same as in Experiment 1. The first drops of ethylene glycol containing catalyst produced an exothermic effect: the temperature rose rapidly to 85°. From 34 g of the ethyl 2-hydroxyethyl acetal and 16.1 g of ethylene glycol in presence of 0.025 g of concentrated hydrochloric acid, there were obtained:

Fraction I, b.p. 48-74° (mainly 73-74°); 29.8 g, n_D^{20} 1.3828
Fraction II, b.p. 73.5-74° at 3 mm; 16.11 g; n_D^{20} 1.4318

Fraction (I) yielded 15 g (67%) of 2-methyl-1,3-dioxolane, b.p. 81.8-82.2°, n_D^{20} 1.3830. Fraction (II) was ethylene glycol. In this case also the rate of the conversion of the ethyl 2-hydroxyethyl acetal into the cyclic acetal is considerably higher than that of the addition reaction, resulting in the isolation of the cyclic acetal:

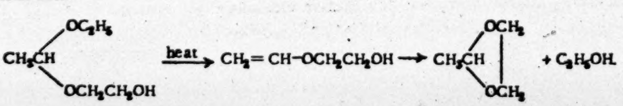


5. Transformation of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal under the Action of Heat

Pure acetaldehyde ethyl 2-hydroxyethyl acetal (34 g) was heated in a stainless steel autoclave for 8 hours at 200-215°; the pressure rose to 15-16 atm. At the end of the reaction 30.1 g of liquid was obtained; it gave the following results on being fractionated:

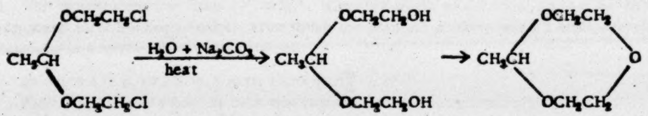
Fraction I, b.p. 52-73°; 4.22 g; n_D^{21} 1.3828
Fraction II, b.p. 73-74°; 27.30 g; n_D^{21} 1.3830
Residue 1.50 g

These results show that simple heating of the ethyl 2-hydroxyethyl acetal leads to its breakdown and to cyclization:

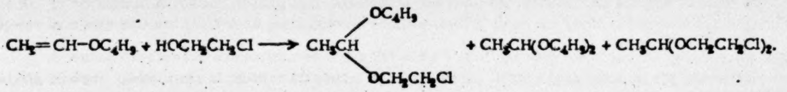


Attempts were made also to prepare the bis(2-hydroxyethyl) acetal and study its reactions.

6. Hydrolysis of Acetaldehyde Bis(2-chloroethyl) Acetal with Sodium Carbonate Solution



The reaction was carried out under the conditions employed for the hydrolysis of 2-chloroethanol in the synthesis of ethylene glycol [13]. The bis(2-chloroethyl) acetal was prepared by the disproportionation of the butyl 2-chloroethyl acetal, which occurs in the course of its synthesis:



$$CH_2{=}CH{-}OC_4H_9 + HOCH_2CH_2Cl \longrightarrow CH_3CH\begin{matrix}OC_4H_9\\ OCH_2CH_2Cl\end{matrix} + CH_3CH(OC_4H_9)_2 + CH_3CH(OCH_2CH_2Cl)_2.$$

The bis(2-chloroethyl) acetal (b.p. 104-105° at 10 mm; d_4^{20} 1.1737; n_D^{20} 1.4529; (47.0 g), Na_2CO_3 (30.0 g), and water (200 ml) were heated in a rotating stainless-steel 500 ml autoclave for 4 hrs 25 min at 140-150° and for 5 hours at 180-190°. Gaseous products (965 ml) were collected, and a clear green liquid smelling of burnt sugar was obtained (259.7 g). The composition of the gaseous products was determined by analysis in an ORS apparatus:

Content of:

air by O_2	28%
CO_2	0%
unsaturated cpd.	0.4%
CO	9.8%
H_2	34.0%
saturated cpd. (by diff.)	27.8%
	100%

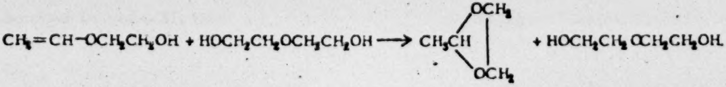
The yield of pure sodium chloride was 26.5 g (89%).

The liquid part was treated as follows. A black resin, which we did not study further, was isolated from the ether extracts. There were no traces of free acetaldehyde present. After numerous fractionations of the aqueous part, in the course of which NaCl separated, 8.15 g of pure ethylene glycol, b.p. 78-79° at 8 mm; n_D^{20} 1.4318, was isolated.

A further experiment on the hydrolysis of the bis(2-chloroethyl) acetal under milder conditions (120-140° for 2 hours and 160-170° for 1 hr 25 min) gave similar results: from 29.7 g of the bis(2-chloroethyl) acetal, 20 g of Na_2CO_3, and 140 ml of water, 6.2 g of ethylene glycol, 550 ml of gaseous products, and some resinous substances were obtained. By the hydrolysis of the bis(2-chloroethyl) acetal, therefore, we did not succeed in obtaining the bis(dihydroxyethyl) acetal, because the reaction did not proceed in accordance with the scheme given above.

7. Reaction of 2-Vinyloxyethanol with Diethylene Glycol

The reaction was carried out in a three-necked flask, as in Experiment 1. One drop of concentrated hydrochloric acid was added to 27 g of diethylene glycol (b.p. 128.5-129° at 8 mm; n_D^{20} 1.4475), stirring was commenced, and 23 g of 2-vinyloxyethanol was added from a dropping funnel over a period of 1 hr 30 min. The reaction was exothermic, but the rise of temperature was slow (from 18° to 30°). The mixture was then set aside for 48 hours. Fractionation yielded 24.6 g (91.2%) of unchanged diethylene glycol, 18.5 g of 2-methyl-1,3-dioxolane (b.p. 81.5-82°; n_D^{20} 1.3982) and 3.07 g of a high-boiling substance having the consistency of glycerol: it decomposed when an attempt was made to distil it at 1.5 mm, and was therefore not studied further. The main reaction in this experiment may therefore be represented by the equation:



8. Reaction of Ethyl Vinyl Ether with Diethylene Glycol

The conditions employed were similar to those of the previous experiment. Ethyl vinyl ether (18 g) was added over a period of 1 hr 10 min to diethylene glycol (26.5 g), which had been carefully mixed with catalyst (HCl). The temperature rose from 16° to 55°. When the whole of the ethyl vinyl ether had been added, stirring was continued for 2.5-3 hours further, after which the reaction mixture was set aside overnight. Vacuum fractionation in a stream of nitrogen yielded:

Fraction I, b.p. to 50° at 3 mm; 12.36 g; n_D^{20} 1.3850
Fraction II, b.p. 98-250° at 3-10 mm (with incipient decomposition); 3.92 g
Residue in flask 23.23 g; n_D^{20} 1.4520

Distillation of Fraction (I) under ordinary pressure yielded 7.85 g of a substance boiling at 75-78° (mainly 78°) (this, after being distilled over $KMnO_4$ + KOH, was found to be ethanol, b.p. 78°, n_D^{20} 1.3618), and 3.2 g of acetaldehyde diethyl acetal, b.p. 103-104° at 758 mm; n_D^{20} 1.3820. An attempt to distil the residue in a high vacuum (0.17-0.19 mm) gave no positive results, since the product began to decompose.

A second experiment was performed under the same conditions with the object of isolating the high-boiling product, taking steps to prevent its partial decomposition. With this in view, at the end of the reaction the low-boiling products were driven off under reduced pressure at temperatures of up to 120°; the residue, after cooling, was extracted several times with absolute ether in order to remove low-boiling compounds and other substances soluble in ether, the bulk of the product being insoluble in ether. Residual ether was removed by treatment in the cold at low pressure with a stream of dry nitrogen that had been passed through alkaline pyrogallol solution, sulfuric acid, and caustic alkali. The low-pressure treatment was continued until constant weight was attained. The product was an almost colorless substance (28 g, i.e. 89.24% on the assumption that the product was the substance (III)); it had the consistency of glycerol, was without odor, and was insoluble in ether, but readily soluble in alcohol and water: d_{20}^{20} 1.1087; d_4^{20} 1.1067; n_D^{20} 1.4600, M (cryoscopic in benzene) found 554.5; 533.7; 541.

Found %: C 53.48; 53.50; H 9.38; 9.49
Calculated %: C 52.59; H 9.16

These results indicate the empirical formula to be $C_{22}H_{46}O_{12}$, the calculated value of M being 502.6. On the basis of this formula, the value found for MR_D is 124.2; MR_D calculated for $C_{22}H_{46}O_{12}$ is 123.276.

Hydrolysis with 2% sulfuric acid gave values of 100.9% and 101.1% $C_{22}H_{46}O_{12}$. These results permit us to ascribe the structure (III) to the product isolated.

9. Reaction of 1,2-Divinyloxyethane with Ethylene Glycol

The object of this experiment was to synthesize the substance (I). The reaction was carried out in a three-necked flask, as in the preceding experiments. Ethylene glycol (15.5 g) containing catalyst was added over a period of 15 minutes to 28 g of 1,2-divinyloxyethane having b.p. 126.8°, n_D^{20} 1.4350; d_4^{20} 0.9220. The temperature in the flask rose from 19° to 77°. When addition of ethylene glycol was complete, stirring was continued for 3.5 hours, and the reaction mixture was then set aside overnight. Vacuum distillation yielded 38.6 g (87.7%) of the cyclic acetal 2-methyl-1,3-dioxolane, b.p. 18.5°/2 mm. After redistillation under atmospheric pressure its constants were: b.p. 82°; n_D^{20} 1.3983; d_4^{20} 0.9798; found MR_D 21.67; calculated for $C_4H_8O_2$ MR_D 21.758.

SUMMARY

1. A study has been made of the reactions of 2-vinyloxyethanol, 1,2-divinyloxyethane, ethyl vinyl ether, and acetaldehyde ethyl 2-hydroxyethyl acetal with ethylene glycol and with diethylene glycol, when heated, and also in presence of catalysts (concentrated HCl).

2. It has been shown that both 2-vinyloxyethanol and the ethyl 2-hydroxyethyl acetal are extremely readily converted into the cyclic acetal 2-methyl-1,3-dioxolane. The second of these reactions proceeds via 2-vinyloxyethanol, which is cyclized under the conditions of reaction.

3. It has been shown that it is possible to apply the disproportionation reaction to the synthesis of high-molecular-weight acetals.

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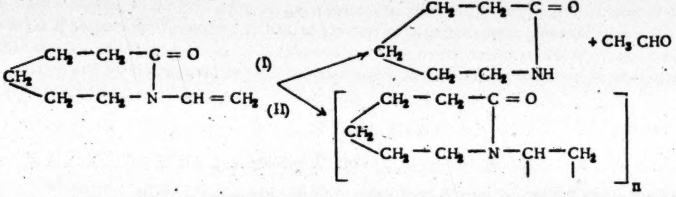
ACTIVATION OF VINYLCAPROLATCTAM IN PRESENCE OF HYDROGEN PEROXIDE

M. F. Shostakovsky and F. P. Sidelkovskaya

One of us [1, 2] has previously suggested that polymerization processes of unsaturated compounds do not constitute an isolated phenomenon, but are very closely associated with other chemical reactions of the original monomers. Air, solvents, and other substances present during polymerization may have important effects [3]. These factors may either encourage the formation of high-polymer products, or, on the contrary, involve the original compounds in other reactions (hydrolysis, alcoholysis, oxidation) and so lower the yield of polymer. The temperature and the concentration and amount of catalyst are also of importance. It has been shown, in the case of vinyl acetate, that the same catalysts (hydrogen peroxide, benzoyl peroxide) not only cause polymerization, but also facilitate addition of alcohols, acids, and water [2].

In a study of the polymerization of vinylcaprolactam in presence of 30% hydrogen peroxide [4] it was found that at 140-150° only polymer formation occured. At 100-125°,, however, not only polymers, but also small amounts of monomeric compounds, caprolactam and acetaldehyde, were found in the reaction products. Their formation may be explained by hydrolysis of the original vinylcaprolactam. As there is very little information in the literature on the question of hydrolysis in presence of peroxides [2], it was considered that a more detailed investigation of this reaction would be of great interest.

In this investigation a study has been made of the reaction of vinylcaprolactam (2-oxo-1-vinylhexamethylenimine) with water in presence of hydrogen peroxide. Actually, in this case two processes proceed simultaneously, namely hydrolysis (I) and polymerization (II):



According to the temperature and ratio of the components, one or other reaction predominates. In a control experiment, in which vinylcaprolactam was heated with water at 100° in absence of hydrogen peroxide, neither polymerization nor hydrolysis products were obtained in detectable amounts: the vinylcaprolactam was recovered unchanged practically completely. It follows that hydrogen peroxide is a catalyst both for the polymerization and for the hydrolysis of vinylcaprolactam. The results of the experiments are given in Tables 1 and 2. It follows from Table 1 that with increase in dilution at constant temperature the percent hydrolysis rises and the percent polymerization falls. On the other hand, at a given dilution (Table 2), with rise in temperature the percent polymerization rises.

TABLE 1

Reaction of Vinylcaprolactam with Water in Presence of H_2O_2 at Constant Temperature and Varying Ratio of Components

Expt. No.	Molar ratio of vinylcaprolactam and water	Temp. of outer bath (°C)	Temp. of reaction mixture (°C)	Yield of polymer (%)	Yield of caprolactam (%)	Total percent conversion
1	1:10	120—130	97—98	19.5	64	83.5
4	1:15	120—135	97—99	15.3	75	90.3
9	1:135	120—135	97—99	7.5	84.5	92.0

Temperature intervals in the range 60 - 100° were investigated. It was not found possible to raise the temperature above 100°, since already at this temperature vigorous boiling of the mass was to be observed. The amount of catalyst and the duration of the experiment were the same in all cases (see Experimental).

TABLE 2

Reaction of Vinylcaprolactam with Water in Presence of H_2O_2 at Constant Ratio of Components and Varying Temperatures

Expt. No.	Molar ratio of vinylcaprolactam and water	Temp. of outer bath (°C)	Temp. of reaction mixture (°C)	Yield of polymer (%)	Yield of caprolactam (%)	Total percent conversion
12	1:135	79—82	60—62	Traces	Traces	Practically 0
11	1:135	100—105	79—82	6	40	46
9	1:135	120—135	97—99	7.5	84.5	92.0
10	1:135	150—160	100	38.9	55.2	94.1

It should be noted that below 100° the general reactivity of vinylcaprolactam in presence of H_2O_2 falls (Experiments nos. 11 and 12, Table 2). By variation of temperature and dilution, therefore, the process may be directed either toward predominant hydrolysis, or toward polymerization.

These experiments confirm the conclusion reached previously [1, 2, 3], that the polymerization of unsaturated compounds, leading to the formation of macromolecular products, is only a special case of the reaction of addition of one organic compound to another. Hence, the course of polymerization processes (particularly in solution) is analogous to that of other addition reactions, being determined both by the nature of the original monomer, and by the nature of the medium and by the physical conditions under which the process is conducted (temperature, light, pressure, catalyst, concentration).

EXPERIMENTAL

Reaction of Vinylcaprolactam with Water in Presence of Hydrogen Peroxide

Vinylcaprolactam (15.9 g) and distilled water (20 ml) were introduced into a three-necked flask fitted with stirrer, thermometer, and reflux condenser attached to three Tishchenko vessels filled with water, and heated in an oil bath. With the temperature of the oil at 120-125° and that of the reaction mixture at 97-98°, small amounts of 28% hydrogen peroxide were added every 1.5-2 hours, the total amount added being 0.51 g, and the duration of the experiment being four hours. Heating was discontinued, nitrogen was blown through the system, and the product was treated as follows: the amount of acetaldehyde was determined by titrating an aliquot part of the reaction mixture and also the contents of the Tishchenko vessels with sodium bisulfite, the calculation being carried out by the formula:

$$A = \frac{2.2\,(B - C)D}{1000E}$$

(A is the amount of acetaldehyde (g), B is the amount of 0.1 N iodine (ml) consumed in a control experiment, C is the amount of 0.1 N iodine (ml) consumed in the working experiment, D is the total amount of solution to be analyzed (ml), and E is the volume of solution taken for analysis (ml)).

As a result of the titration it was found that there was 1.15 g acetaldehyde in the main reaction product, and 0.44 g in the solution from the absorption vessels: 1.59 g of acetaldehyde in all. This amount of acetaldehyde corresponds to 5 g (32%) of the original vinylcaprolactam *.

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* In this and succeeding experiments, in spite of all precautions taken, it was not found possible to account for the whole of the acetaldeyde. It is evidently partly lost when the separate portions of catalyst are introduced into the reaction mixture. It is necessary to estimate the degree of hydrolysis by the amount of caprolactam isolated.

The main reaction product was fractionated, first at atmospheric pressure, and then under reduced pressure; the following fractions were obtained:

Fraction I, b.p. 40-95°/755 mm; 0.8 g
Fraction II, b.p. 29-40°/29 mm; 17.9 g; n_D^{15} 1.3385
Fraction III, b.p. 117-120°/5 mm; 7.7 g; n_D^{15} 1.4760
Resinous residue; 4.35 g

Fraction I had the sharp odor of acetaldeyde: it was an aqueous solution of this substance: 0.4 g of Fraction I was added to a solution of 0.1 g of 2,4-dinitrophenylhydrazine in 5 ml of 10% hydrochloric acid, when orange crystals of the 2,4-dinitrophenylhydrazone of acetaldehyde (m.p. from alcohol, 162 - 163°, not depressed in admixture with authentic sample) came down. Fraction II consisted mainly of water. Fraction III readily crystallized out in the condenser: the crystals were transferred to a flask having a sword-shaped side tube and were distilled, yielding 7.3 g of caprolactam, m.p. 64-67° (68-69° after recrystallization from dry ether; the literature [5] gives 68-70°); in admixture with pure caprolactam there was no depression in melting point. The resinous residue (4.3 g) was dissolved in 10 ml of benzene and reprecipitated with 100 ml of diethyl ether. The product was 2 g of polyvinylcaprolactam in powder form. By fractionation of the benzene solution, a further 1 g of crystalline caprolactam (m.p. 66-68°) was isolated, and also a further 1 g of resinous polymer. As has already been shown [4], the latter was a mixture of pure polymer (in the form of powder) and monomer. In order to characterize the polyvinylcaprolactam, its specific viscosity η_{sp} and molecular weight were determined.

The specific viscosity η_{sp} (1 g of polymer in 100 ml of benzene) was 0.2079. The molecular weight, determined cryoscopically in benzene, varied over the range 3000-5000.

The remaining experiments on the polymerization of vinylcaprolactam in aqueous solution in presence of hydrogen peroxide, and also the treatment of the reaction products, were carried out by the procedure described above. The ratio of components and the temperature were varied. In all these experiments the time was four hours, the amount of hydrogen peroxide (28%) added was 0.52 g, and the amount of vinylcaprolactam taken was 10-12 g.

SUMMARY

The reaction of vinylcaprolactam with water in presence of hydrogen peroxide has been studied, and it has been shown that two process occur: hydrolysis and polymerization. With rise in temperature and reduction in dilution the percent polymerization increases and the percent hydrolysis diminishes.

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DEPOLYMERIZATION OF DICYCLOPENTADIENE BY THE CONTINUOUS METHOD

N. F. Kononov, Z. Ya. Lapshina, and S. S. Novikov

In recent years a number of papers devoted to the search for means of utilizing cyclopentadiene for the preparation of various substances have appeared in the literature [1-3]. In this connection the problem of developing accessible and convenient methods for the preparation of this valuable hydrocarbon becomes of particular importance. It is well known that up to the present time the main source of cyclopentadiene has been its dimer, which is formed as a by-product of the coal-tar industry or by the pyrolysis of petroleum products [2].

In order to prepare cyclopentadiene from its dimer, the latter is generally depolymerized by heating at 175-180°, with simultaneous distillation of the monomer formed [3]. This method, in spite of its wide use, has a number of disadvantages. In the first place, it is inconvenient because of its low productivity (only 40-60 g of monomer is obtained per hour from one liter of reaction vessel space. Furthermore, in the intermittent method of preparing cyclopentadiene, part of the dimer, owing to the effect of prolonged heating, is converted into more complex polymers, and the yield of monomer is therefore reduced.

Baur and Frater [4] determined the equilibrium constants for the depolymerization process over the range 149 - 193°. Values of 277, 591, 742, 1177, and 2200 were found for the temperatures 149°, 165°, 170°, 180°, and 195° respectively. The rate of the unimolecular reaction for the decomposition of the dimer is higher in this temperature range than that of the bimolecular dimerization reaction, and decomposition proceeds practically to completion. The rate constant for the decomposition reaction in the liquid phase has been determined by Wasserman for temperatures in the range 79-150°.

$$k = 6 \cdot 10^{12} e^{-(34000/RT)} .$$

In the temperature range cited above the heat of reaction for the decomposition has been found to be 12.3 kcal per mole [5].

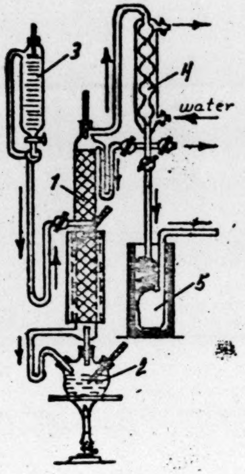
On the basis of this information we carried out experiments with the object of developing a continuous method of decomposing the dimer. It was essential that the following conditions should be fulfilled: 1) a minimum period of contact of dimer with the heated surface; 2) rapid supply of heat to the reaction zone; 3) fractional condensation of dimer carried away by the vapor of the cyclopentadiene formed.

These requirements were satisfied by the apparatus represented in the figure. The apparatus consisted of a glass column 1, height 700 mm, diameter 30 mm, having a filling of short sections of glass tube, diameter 5 mm, average length 5 mm. The lower part of the column, height 500 mm, was the reactor, and was provided with a spiral winding for heating. The higher part of the column served as a fractionating column with air cooling. The dimer entered continuously, from the reservoir 3, through a perforated glass tube into the upper part of the reactor. The lower part of the column communicated with a vessel 2, which served for the decomposition of residues of dimer. Experiment showed that with suitable regulation of the supply of dimer the decomposition was generally complete in the column. In the upper part of the column the separation of entrained dimer from cyclopentadiene vapor took place. The vapor then passed further to a water-cooled condenser 4, and the condensed cyclopentadiene collected in the receiver 5, which was cooled with ice.

When the reaction conditions had been established, the apparatus continued to work for a day or so. The yield of monomer was 99 % of the dimer passed. The productivity of the reactor was 150 g per liter of reaction space.

Formation of higher polymers of cyclopentadiene occured only to a very slight extent; it nevertheless took place, and it was therefore necessary to stop the process periodically to free the apparatus from resins formed on the walls in a thin layer that hindered heat transfer. On the average a stop was made after 100 - 150 hours of continuous operation.

On very rare occasions, when the supply of dimer was increased (at 200° the supply was generally 50 - 60 ml per hour), it was not fully separated in the fractionation column and was drawn by monomer vapor into the condenser, which was indicated by the thermometer and also by the change in the refractive index of the monomer. In such a case the supply of dimer was diminished, and the monomer, containing dimer impurity was directed into the fractionation column, from which it passed to the decomposition zone. When vapor of monomer free from dimer passed from the column, the supply of fresh dimer for decomposition was renewed.



Apparatus: 1—column; 2—still flask; 3—measuring reservoir; 4—condenser; 5—receiver.

As an example we will give the figures for a typical experiment, which lasted for 12 hours. For the decomposition, 582.6g of dimer was taken- it had the following constants: b. p 58-60° at 14 mm, n_D^{20}, 1.5125; d_4^{20} 0.9772 calculated MR_D 40.84, found MR_D 40.56. The decomposition temperature was maintained in the range 195-200°. The product was 575.6 g of monomer having the following constants: b.p. 40-42°; n_D^{20} 1.4446; d_4^{20} 0.8016; calculated MR_D 22.16; found MR_D 21.87. Thus the undoubted advantages of the continuous method of preparing monomer over the intermittent method have been demonstrated, and a simple apparatus for carrying out the process has been proposed.

In conclusion the authors consider it to be their pleasant duty to express their thanks to N.I. Shuikin for valuable advice in the course of the performance of this work.

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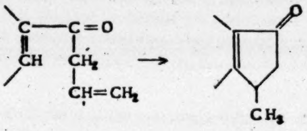
INVESTIGATION OF THE MECHANISM OF CYCLIZATION WITH THE AID OF DEUTERIUM

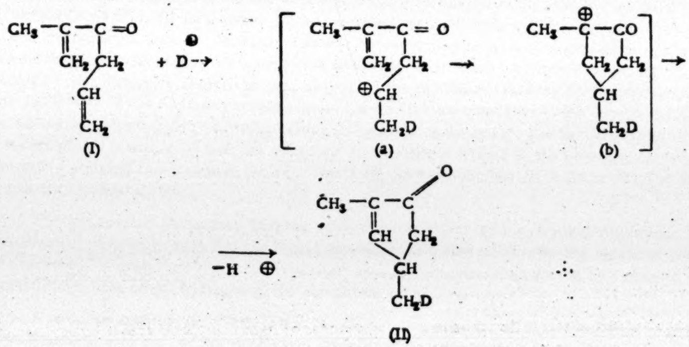
COMMUNICATION 1. CYCLIZATION OF 2-METHYL-1,5-HEXADIEN-3-ONE

D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya, and I. N. Nazarov

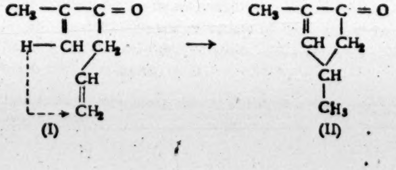
The investigations of Nazarov and coworkers have shown that substituted 1,5-hexadien-3-ones are readily cyclized in presence of acids, giving substituted cyclopentenones [1]:



In explanation of these reactions Nazarov proposed an ionic mechanism [2], according to which the reaction is intermolecular and commences with the addition of a hydrogen ion to the molecule of the ketone undergoing cyclization. This concept corresponds, for example, to Scheme 1, according to which the first stage of the process is the addition of a proton (in Scheme 1, a deuteron) at the terminal carbon of the allyl radical, with formation of a carbonium ion (a); this then cyclizes to give the cyclic ion b, which loses a proton with formation of 2,4-dimethyl-2-cyclopenten-1-one (in Scheme 1, 2-methyl-4-methyl-d-2-cyclopenten-1-one). Scheme 1 is as follows:



However, the possibility cannot yet be excluded that cyclization proceeds by intramolecular transfer of a transfer of a hydrogen atom (Scheme 2):



We hoped to prove the mechanism of this reaction by carrying out the cyclization in presence of deuterium-rich phosphoric acid. In that case, if the mechanism proposed by Nazarov were correct, then it follows from Scheme 1 that the dimethylcyclopentenone obtained would contain deuterium. This method of proof, however, is possible only when the original dienone (I) and the cyclic ketone II are unable, under the conditions of the experiment, to exchange their hydrogen atoms for deuterium, or when they exchange them so slowly that this exchange can be taken into account.

It is well known that, under suitable conditions, ketones in contact with deuterium oxide are unable to exchange hydrogen in the α-position to the carbonyl group for deuterium [3]. These exchange reactions are generally carried out in presence of alkaline catalysts, but cases are known also of the acid catalysis of these reactions [4]. Our first problem, therefore, was to investigate the tendency of the dimethylcyclopentenone II to undergo deuterium exchange under the conditions under which the cyclization of 2-methyl-1,5-hexadien-3-one (I) was performed. Our experiments showed that exchange of hydrogen atoms of the dimethylcyclopentenone for deuterium proceeds only extremely slowly (Table 1). We then carried out the cyclization, under the same conditions, of 2-methyl-1,5-hexadien 3-one (I)) in presence of deuterium-rich phosphoric acid. It was found that the dimethylcyclopenteenone obtained (II) contained considerably more deuterium than in the previous experiments (Table 2).

The results of these preliminary experiments were in agreement with the intermolecular ionic mechanism for the reaction (for example, that given in Scheme 1), but did not constitute a complete proof, since the possibility had not been excluded that the original 2-methyl-1,5-hexadien-3-one entered into an exchange reaction considerably more readily than the dimethylcyclopentenone, thus explaining the enhanced deuterium content of the cyclic ketone obtained.

In order to obtain a complete proof of the reaction mechanism it was necessary to study the tendency for the methylhexadienone to undergo exchange under the precise conditions of the cyclization reaction. For this purpose it was necessary to find conditions under which only part of the methylhexadienone would be converted into the dimethylcyclopentenone, i. e. under which the cyclization reaction would not proceed to completion. The recovered methylhexadienone and the dimethylcyclopentenone obtained would have to be examined for thier deuterium contents. An excess of deuterium in the cyclic ketone could in this case be explained only by its introduction in the process of cyclization, and would thus form a convincing proof of the mechanism of this reaction. From the experimental side, however, this method of proof met with considerable difficulties: thus the boiling points of the ketones (I) and (II) differ only by 7.5° at 40 mm, and in order to separate them a highly efficient column working at a constant low pressure was required. Another difficulty was that of choosing conditions for incomplete cyclization (Table 3). After a number of experiments, however, these conditions were found. Incomplete-cyclization experiments in presence of deuterium-rich phosphoric acid showed, in the first place, that the methylhexadienone showed no appreciable tendency to undergo exchange under the cyclization conditions: the density excess of the water from the combustion of 2-methyl-1,5-hexadien-3-one in Experiment 9 was 15γ, and in Experiment 10 it was 32 γ. In the second place, it was found that the dimethylcyclopentenone formed in the course of incomplete cyclization was appreciably enriched in dueterium. In Experiment 10, for example, the combustion water of the dimethylcyclopentenone had a density excess of 190γ.

The results cited above show that the cyclization reaction is accompanied by introduction of deuterium from the deuterium-rich phosphoric acid into the cyclic ketone formed, thus confirming the reaction mechanism proposed by Nazarov. The enrichment in deuterium of the cyclic ketone was, however, less than that to be expected on the basis of the isotopic composition of the hydrogen of the phosphoric acid.

A probable explanation of this is that the dissociation constant of light phosphoric acid is higher than that of heavy phosphoric acid and, at the same time, the rate of the addition of a proton is higher than that of a deuteron. Another possible explanation is that the intermolecular mechanism of cyclization is to some extent accompanied by the intramolecular mechanism (Scheme 2). In order to solve this question we carried out the cyclization of 2-methyl-1,5-hexadien-3-one in presence of practically pure phosphoric acid-d_3. The cyclic ketone obtained under these conditions corresponded very closely in its isotopic composition to monodeuteriodimethylcyclopentenone, i. e. in this case practically exactly one atom of deuterium entered into the molecule of the cyclopentenone. It was thus shown that the intermolecular cyclization mechanism was the only one possible, and Nazarov's postulate of an ionic intermolecular mechanism for this reaction was thus confirmed.

It is possible to obtain more detailed information about the mechanism of this reaction by determining the position of the deuterium atom in the cyclic ketone.

EXPERIMENTAL

Investigation of Hydrogen Exchange in Dimethylcyclopentenone

Dimethylcyclopentenone was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one and the corresponding methoxy ketones in presence of phoshoric acid, and after distillation through a column it had the following constants: b. p. 77.0 -77.5°/37mm and $n_D^{20.2}$ 1.4670. In the study of the deuterium exchange, the dimethylcyclopenten was introduced into a two-necked flask together with an equal weight of phosphoric acid (sp. gr. 1.79) enriched in deuterium. At the end of the experiment the reaction mixture was poured into an aqueous solution of sodium bicarbonate, extracted with ether, dried with magnesium sulfate, and distilled from a small Favorský flask. The main fraction had b.p. 46.0 -42.0/10 mm and n_D^{20} 1.4673. The conditions and results of the experiments are given in Table 1.

TABLE 1

Expt. No.	Temp. (°C)	Time (hr)	Initial equiv. density excess of phosphoric acid (γ)	Calcd. density excess for exchange of 2H (γ)	Density excess found (γ)	Exchange (% of calcd. value)
1	24	24	25600	3905	775	20
2	19	20	25600	3985	650	16
3	20	2	8630	1020	31	3

From these experiments it will be seen that exchange between dimethylcyclopentenone and heavy phosphoric acid proceeds only very slowly. Under the conditions of Experiment 3 practically no exchange occurred.

Cyclization of 2-Methyl-5-hexadien-3-one in Presence of Heavy Phosphoric Acid.

The 2-methyl-1,5-hexadien-3-one used in the experiment had b.p. 36 - 57°/21 mm and $n_D^{20.2}$ 1.4760. The cyclization was performed in presence of an equal weight of phosphoric acid (sp. gr. 1.79) having an equivalent density excess of 9340 γ. The results of the experiment are given in Table 2.

TABLE 2

Expt. No.	Temp. (°C)	Time (hr)	Calcd. density excess (γ) for the change of		Density excess found (γ)
			2H	1H	
4	19	20	4045	2260	2615

It will be seen that the cyclization product in this experiment is highly enriched in deuterium in comparison with those of Experiments 1-3.

Fractionation through a Column of a Mixture of 2-Methyl-1,5-hexadien-3-one and Dimethylcyclopentenone

In the preparation of 2-methyl-1,5-hexadien-3-one from the corresponding compounds by removal of methanol (heating with p-toluenesulfonic acid), partial cyclization into dimethylcyclopentenone occurs. Similar phenomena have been observed previously by Nazarov and coworkers in other cases [5]; For fractionation through a column we took the mixture of ketones obtained by splitting methanol from the methoxy compounds corresponding to 2-methyl-1,5-hexadien-3-one in presence of p-toluensulfonic acid. We used a column made up of single turns of glass spirals having an efficiency at ordinary pressure of 25 theoretical plates and provided with a manostat. The fractionation curves clearly showed that it was possible to separate these ketones with the aid of this column. The amount of the ketone mixture taken for fractionation was 60 g. and the following fractions were obtained:

Fraction I, head fraction collected to 71.5° / 39 mm; $n_D^{20.2}$ 1.4690, weight 8.5 g.
Fraction II, 2-methyl-1,5-hexadien-3-one, b.p. 71.5°/39 mm; $n_D^{20.2}$ 1.4730; weight 18.2 g.
Fraction III, intermediate, $n_D^{20.2}$ 1.4690; weight 7.2 g
Fraction IV, dimethylcyclopentenone, b.p. 79.4° at 39 mm; $n_D^{20.2}$ 1.4679; weight 6.7 g.
Fraction V, b.p. 79.5-87.1°, $n_D^{20.2}$ 1.4572, weight 1.8 g.
Residue, 14.0 g.

TABLE 3

Determination of the Conditions for the Incomplete Cyclization of 2-Methyl-1,5-hexadien-3-one.

Expt. no.	Sp. gr. of phosphoric acid	Temp. (°C)	Time (hrs.)	Results of experiments
5	1.75	20	3	Cyclization did not go
6	1.798	22-23	3	Cyclization went completely
7	1.790	20	1	Cyclization did not go
8	1.798	20-21	1.7	Cyclization went to the extent of 50% (judging only from the refractive index)

The fractionation curve is given in Fig. 1.

Fraction II (2-methyl-1,5-hexadien-3-one) was redistilled through the same column. The main fraction had b.p. 72.0° at 42 mm; $n_D^{20.2}$ 1.4738, d_4^{20} 0.8897 (Fig. 2).

Fraction IV (dimethylcyclopentenone) was also redistilled through the column. The main fraction had b.p. 77.0-77.5° at 37 mm; $n_D^{20.3}$ 1.4670; d_4^{20} 0.9367.

Incomplete Cyclization of 2-Methyl-1,5-hexadien -3-one in Presence of Heavy Phosphoric Acid

Experiment 9. To stirred 2-methyl-1,5-hexadien-3-one (22.4 g) contained in a three-necked flask, phosphoric acid (21.3 g; sp.gr. 1.794) having an equivalent density excess of 8630 γ was added carefully; the flask was cooled with ice water, and the temperature did not exceed 7°. When addition of phosphoric acid was complete, the flask was placed in a thermostatic water bath, and the temperature in the flask was maintained within the range 20-21° for 1 hour 45 minutes. At the end of this period the reaction mixture was poured into a bicarbonate solution, and was then extracted with ether and dried with magnesium sulfate. After being distilled in order to remove resin, the mixture of reaction products was fractionated through a column. The amount taken for distillation through the column was 13.7 g, and the following fractions were obtained:

Fraction I, b.p. 62.5-67.2° at 35 mm; 1.3 g
Fraction II, b.p. 67.2-67.5° at 35 mm; 4.2 g.

Fraction II was pure 2-methyl-1,5-hexadien-3-one, $n_D^{20.1}$ 1.4730. It was not found possible to distill the residue through the column. It was transferred to a small Favorsky flask and vacuum-distilled. The substance had an extended boiling range, 73-80°/35 mm; n_D^{20} 1.4705, and was evidently a mixture of 2-methyl-1,5-hexadien-3-one and dimethylcyclopentenone, in which, according to the refractive index, 45% of dimethylcyclopentanone was present.

The 2-methyl-1,5-hexadien-3-one was burnt, and the combustion water was purified by the method adopted in our laboratory [6]. The density excess of the combustion water was found to be 15 γ. The calculated density excess for an exchange of 2H was 1040 γ. The mixture of ketones (b.p. 73-80°/35 mm) was also burnt, and the resulting water had a density excess of 112 γ. By taking into consideration the percentage composition of the ketone mixture and also the fact that the 2-methyl-1,5-hexadien -3-one was only slightly enriched in deuterium, an approximate calculation of the density excess of the combustion water from the dimethylcyclopentenone present could be made; the value found was 215 γ.

Experiment 10. In this experiment 40.85 g of 2-methyl-1,5-hexadien-3-one and 37.90 g of phosphoric acid having a density excess of 8630 γ were taken. Addition of phosphoric acid was carried out as in the preceding experiment. In the course of the experiment the temperature varied from 18° to 20.5°, and the experiment lasted for 2 hours 25 minutes. The reaction mixture was then treated as in the preceding experiment. The residue after removal of ether was vacuum-distilled: it came over completely between 42° and 68° at 8 mm. The distillate was distilled through a column, and after the head fraction 15.2 g of 2-methyl-1,5-hexadien-3-one (I), b.p. 69.5-70°/36 mm and n_D^{18} 1.4737 was obtained. After a small intermediate fraction (0.8 g), 3.5 g of 2,4-dimethyl-2-cyclopenten-1-one (II), b.p. 75.2-76.5°/35-36 mm and $n_D^{20.6}$ was obtained.

The density excess of the combustion water from 2-methyl-1,5-hexadien -3-one was 32 γ. For exchange of 2H, the density excess should have been 1110 γ. The density excess of the combustion water from dimethylcyclopentenone was 190 γ.

Cyclization of 2-Methyl-1,5-hexadien- 3-one in Presence of Phosphoric Acid-d_3

Experiment 11. Phosphoric acid-d_3 (sp. gr. 1.76; equivalent density excess 91,000 γ) was added gradually to 4.02 g of 2-methyl-1,5-hexadien 3-one. The reaction mixture reamined at 20-21° for 3 hours 30 minutes; it was treated as in the preceding experiments. The dimethylcyclopentenone obtained was distilled off from resin and distilled from a Favorsky flask (b.p. 45-46°/9 mm, $n_D^{18.2}$ 1.4670). It may be considered from the constants that the cyclization reaction went to completion. The density excess of the combustion water from the ketone was 8290 γ. The value calculated for the exchange of one hydrogen atom was 7765 γ.

SUMMARY

1. It has been shown that 2,4-dimethyl-2-cyclopenten-1-one and 2-methyl-1,5-hexadien-3-one do not undergo appreciable protium-deuterium exchange when placed in contact with heavy phosphoric acid for two hours at 20°.

2. It has been shown that in the cyclization of 2-methyl-1,5-hexadien-3-one in presence of heavy phosphoric acid (sp.gr. 1.79) at 20° the dimethylcyclopentenone obtained is appreciably enriched in deuterium.

3. It has been shown that in the cyclization of 2-methyl-1,5-hexadien-3-one in presence of pure phosphoric acid-d_3 a monodeuteriodimethylcyclopentenone is obtained.

4. It follows from the experimental results obtained that the cyclization of 2-methyl-1,5-hexadien-3-one is accompanied by the introduction of one deuterium atom into the dimethylcyclopentenone molecule formed, and this constitutes a proof that the cyclization reaction has an intermolecular ionic mechanism, as proposed by Nazarov.

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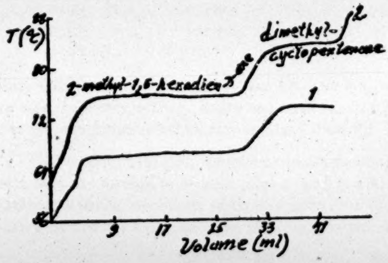

Fig. 1. Fractionation curves of a mixture of 2-methyl-1,5-hexadien-3-one and dimethylcyclopentenone: 1) pressure 31 mm; 2) pressure 39 mm.

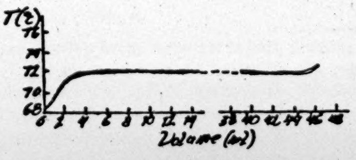

Fig. 2. Fractionation curve for 2-methyl-1,5-hexadien-3-one; pressure 42 mm.

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ORGANOPHOSPHORUS COMPOUNDS:
O,O-DIALKYL HYDROGEN PHOSPHOROTHIOLOTHIONATES

M. I. Kabachnik and T. A. Mastryukova

In an investigation of the reaction of tetraphosphorus heptasulfide P_4S_7 with alcohols, we found [1] that one of the products was an O,O-dialkyl hydrogen phosphorothiolothionate $(RO)_2PSSH$, which we obtained as a colorless liquid that could be distilled under reduced pressure. This group of substances has already been known for about a century. They were first obtained in 1859 by Carius [2] by the reaction of alcohols with phosphorus "pentasulfide", but Carius proposed an incorrect equation for this reaction. Later, Pishchimuka [3] verified the work of Carius and found that practically the only organophosphorus compounds formed in this reaction are the 0,0-dialkyl hydrogen phosphorothiolothionates; Pishchimuka also gave the correct equation for this reaction [4]. In 1945 Mastin and coworkers [5] confirmed that the structure of these phosphorothiolothionates was in accord with the formula $(RO)_2PSSH$. Finally, O,O-dialkyl hydrogen phosphorothiolothionates and their salts have been described in numerous patents.

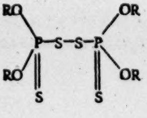
All the workers who have previously prepared O,O-dialkyl hydrogen phosphorothiolothionates have described them as undistillable sirups, have not analyzed them, and have characterized them only in the form of their salts. Our preparation of these phosphorothiolothionates in the form of colorless liquids that could be vacuum-distilled caused us to doubt the identity of the dialkyl hydrogen phosphorodithioates obtained from the phosphorus sulfides P_4S_7 and P_4S_{10}. We repeated the reaction of the decasulfide P_4S_{10} with alcohols and found, in complete agreement with the results of Pishchimuka, that the main products were O,O-dialkyl hydrogen phosphorothiolothionates. Again, however, colorless liquids that could be vacuum-distilled were obtained, and their description on many occasions as undistillable sirups must be considered to be a misunderstanding. We, therefore, have obtained these substances in the pure form for the first time. We give a table showing the properties of O,O-dialkyl hydrogen phosphorothiolothionates obtained from the phosphorus sulfides P_4S_7 and P_4S_{10} (Table 1).

TABLE 1

Formula	Prepared from	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	Yield (%)
$(CH_3O)_2PSSH$ . . .	P_4S_{10}	62-63	4.5	1.2888	1.5343	73.2
$(C_2H_5O)_2PSSH$. . .	P_4S_{10}	81-82	5	1.1654	1.5076	76.5
$(C_2H_5O)_2PSSH$. . .	P_4S_7	97-98	12	1.1650	1.5105	15.4
$(n\text{-}C_3H_7O)_2PSSH$.	P_4S_{10}	81.5-82.5	2	—	1.4986	75.0
$(n\text{-}C_3H_7O)_2PSSH$.	P_4S_7	85-86	3	1.1040	1.4987	6.5
$(i\text{-}C_3H_7O)_2PSSH$. .	P_4S_{10}	71-72	3	1.0911	1.4918	60.0
$(i\text{-}C_3H_7O)_2PSSH$. .	P_4S_7	70.5-71.5	3	1.0913	1.4920	25.4

There is complete agreement between the constants of the O,O-dialkyl hydrogen phosphorothiolothionates obtained from the two sulfides P_4S_7 and P_4S_{10}. The dibutyl compound was the only one of the esters that was not successfully vacuum-distilled, and this was therefore isolated as its mercury salt, m.p. 60-61°. The melting points of the mercury salts prepared from the sulfides P_4S_7 and P_4S_{10} were identical, and a mixed test showed no depression. In the same way the corresponding single and mixed melting points were identical for salts prepared from the distillable phosphorothiolothionates obtained from P_4S_7 and P_4S_{10} (Table 2).

O,O-Dialkyl hydrogen phosphorothiolothionates are colorless highly refractive liquids, smelling of hydrogen sulfide; they are soluble in organic solvents and in alkalis, and the lower members are soluble in water. They may be titrated as strong monobasic acids in aqueous and alcholic medium. O,O-Dialkyl hydrogen phosphorothiolothionates are readily oxidized in an alkaline solution of iodine with formation of the corresponding disulfides:



We prepared disulfides having R = CH_3, C_2H_5, and $i\text{-}C_3H_7$. They are water-insoluble crystalline substances.

TABLE 2

Formula	M.p. (°C)		
	this work		Data in the literature
	from P_4S_7	from P_4S_{10}	
$[(CH_3O)_2PSS]_2Ni$ . .	–	124-125	123° [6]
$[(C_2H_5O)_2PSS]_2Pb$ . .	75-76	75-76	74° [3,5]
$[(i\text{-}C_3H_7O)_2PSS]_2Pb$.	130-131	130-131	–
$[(n\text{-}C_4H_9O)_2PSS]_2Hg$.	60-61	60-61	61-62° [5]

TABLE 3

Formula	Equivalent	
	Found	Calc.
$(CH_3O)_2PSSH$ . . .	161.3; 161.2	158
$(C_2H_5O)_2PSSH$ . .	188.8; 189.0	186
$(n\text{-}C_3H_7O)_2PSSH$.	216.6; 216.7	214
$(i\text{-}C_3H_7O)_2PSSH$. .	216.7; 217.5	214

EXPERIMENTAL

Reaction of the Decasulfide P_4S_{10} with Alcohols

The anhyrous alcohol was introduced into a round-bottomed flask having a two-way adapter connected to a reflux condenser protected with a calcium chloride tube, and the phosphorus sulfide was added in small portions. The lower alcohols reacted vigorously, but heating was required for the reaction of butyl alcohol with the decasulfide P_4S_{10}. The mixture was heated in a water bath until evolution of hydrogen sulfide ceased (for butyl alcohol this required 7-8 hours' heating). The reaction mixture was then filtered, if necessary, and fractionated, first at atmospheric pressure and at 30-40 mm to remove the alcohol, after which the reaction product was vacuum-distilled.

O,O-Dimethyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{10} (33.3 g) and methyl alcohol (24.0 g). The whole of the phosphorus sulfide reacted, practically without residue. The fractions obtained at 4.5 mm were:

Fraction I, b.p. 41-62°; 3.5 g
Fraction II, b.p. 62-63°; 34.7 g (yield 73%)
Fraction III, b.p. 63-71°; 5.1 g

For Fraction II: n_D^{20} 1.5343; d_4^{20} 1.2888; σ_{20} 38.87; found MR_D 38.13; calculated MR_D 38.34.

Found %: P 19.51, 19.60; Parachor 306.1
$C_2H_7O_2PS_2$. Calculated %: P 19.62; Parachor 303.0

Nickel Bis(O,O-dimethyl Phosphorothiolothionate $[(CH_3O)_2PSS]_2Ni$. Nickel chloride (1.29 g) was added to a neutralized solution of O,O-dimethyl hydrogen phosphorothiolothionate (3.16 g), and the dark-colored solution was evaporated to dryness. The nickel salt was separated from sodium chloride by recrystallization from benzene, and 3.5 g of nickel bis(O,O-dimethyl phosphorothiolothionate) was obtained in the form of glistening leaves of a bright lilac color, m.p. 124-125° (literature gives 123° [6]).

O,O-Diethyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{10} (50.8 g) and ethyl alcohol (69.0 g). The solid residue after the reaction weighed 3.2 g, and 65.1 g (76.5%) was obtained of a substance of b.p. 81.5-82.5°/5 mm; n_D^{20} 1.5076; d_4^{20} 1.1654; σ_{20} 31.7; found MR_D 47.54; calculated MR_D 47.58.

Found: Parachor 378.7
$C_4H_{11}O_2PS_2$. Calculated: Parachor 379.8.

The constants of the same substance, obtained from P_4S_7 [1], had b.p. 97-98° at 12 mm; n_D^{20} 1.5105; d_4^{20} 1.1650; σ_{20} 31.7.

Lead Bis(O,O-diethylPhosphorothiolothionate) $[(C_2H_5O)_2PSS]_2Pb$. This was prepared as previously described [1]. M.p. 75-76° (from alcohol). Mixed test with lead salt obtained from P_4S_7 [1] and according to Martin [5] gave the result: 75-76°.

O,O-Dipropyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{10} (11.1 g) and propyl alcohol (12 g). There was no residue, and 16.1 g (75.0%) was obtained of a substance of b.p. 81.5-82.5°/2 mm and n_D^{20} 1.4986. The constants of the thio ester $(n\text{-}C_3H_7O)_2PSSH$ obtained from P_4S_7 were b.p. 85-86°/3 mm and n_D^{20} 1.4987.

O,O-Diisopropyl Hydrogen Phosphorothiolothionate. This was prepared from 5.6 g of P_4S_{10} and 6 g of isopropyl alcohol. There was no residue, and 6.4 g (60%) of the diisopropyl hydrogen phosphorothiolothionate, b.p. 71-72° at 3 mm and n_D^{20} 1.4918, was obtained. The constants of the thio ester $(i\text{-}C_3H_7O)_2PSSH$ obtained from P_4S_7 were b.p. 70.5-71.5° at 3 mm, n_D^{20} 1.4920 [1].

Lead Bis(O,O-diisopropyl Phosphorothiolothionate) $[(i\text{-}C_3H_7O)_2PSS]_2Pb$. O,O-Diisopropyl hydrogen phosphorothiolothionate (4.28 g) was neutralized with caustic soda (phenolphthalein), and the solution was mixed with lead acetate (3.79 g). White curds (7.4 g) were obtained. Two crystallizations from alcohol yielded 5.1 g of the lead salt in the form of fine silky snow-white needles, m.p. 130-131°. The melting point of the lead salt obtained in the same way from P_4S_7 [1] was 130-131°, and a mixed test gave no depression.

Found %: S 24.95; 25.17

$C_{12}H_{28}O_4P_2S_4Pb$. Calculated %: S 25.00

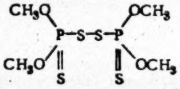
Mercury Bis(O,O-dibutyl Phosphorothiolothionate). The substances taken were P_4S_{10} (11.1 g) and butyl alcohol (14.8 g); there was no residue. The dark-colored reaction mixture was neutralized with 10% caustic soda, the small amount of oil that separated as a layer was removed, and the aqueous layer was washed with ether. Mercuric chloride (12 g) was then added, and the mercury salt was precipitated from the aqueous solution in the form of an oil. It was extracted with ether, and the ether extract was dried over calcium chloride. After evaporation of the ether, 25 g of salt, m.p. 56-58°, was obtained. The melting point after recrystallization from methyl alcohol was 60-61°. The melting points of the same salt prepared from P_4S_7 [1] and according to Mastin [5] were 60-61° and 61-62° respectively. Mixed tests showed no depression (60-60.5°).

Titration of O,O-Dialkyl Hydrogen Phosphorothiolothionates

All of the phosphorothiolothionates were readily soluble in a sufficiently large amount of titration alkali, the excess of which could be exactly back-titrated. The following titration results were obtained (Table 3).

Oxidation of the O,O-Dialkyl Hydrogen Phosphorothiolothionates with Iodine

The disulfide

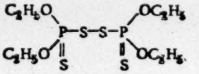


was obtained as follows: O,O-dimethyl hydrogen phosphorothiolothionate (4.8 g) was dissolved in an equivalent amount of aqueous caustic soda. A solution of iodine (3.8 g) in aqueous potassium iodide was added. The yellowish precipitate that formed was filtered off and dried (4.5 g, m.p. 48-49.5°), and was then recrystallized from hexane, yielding 3.5 g (74.3%) of the disulfide, m.p. 51-52°, a substance that is soluble in organic solvents, but insoluble in water.

Found %: C 15.50; 15.32; H 3.61; 3.56; P 19.57; 19.59; S 40.20; 40.26

$C_4H_{12}O_4P_2S_4$. Calculated %: C 15.29; H 3.82; P 19.74; S 40.76

The disulfide

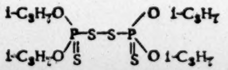


was prepared similarly to the previous one from 9.3 g of O,O-diethyl hydrogen phosphorothiolothionate and 6.39 g of iodine. It came down as an oil and was extracted with ether; the ether solution was dried over sodium sulfate, and the ether was evaporated off. The residue crystallized out when cooled with dry ice. The crystals were filtered off and washed well with hexane. The product, 4.3 g (48%) of cubic crystals, was readily soluble in organic solvents and insoluble in water.

Found %: P 16.84; 16 89

$C_8H_{20}O_4P_2S_4$. Calculated %: P 16.76

The disulfide



was prepared similarly to the previous one from 8.5 g of O,O-diisopropyl hydrogen phosphorothiolothionate and 5 g of iodine in neutral aqueous solution. It came down as a colorless curdy finely crystalline precipitate. The yield of crude product was 8.3 g (97.4%); yield after recrystallization from ethyl alcohol 7.05 g (82.75%); m.p. 91-92°, not changing after a second crystallization. Soluble in organic solvents.

Found %: C 33.84; 33.74; H 6.53; 6.56; P 14.54; 14.48; S 29.28; 29.24

$C_{12}H_{28}O_4P_2S_4$. Calculated %: C 33.80; H 6.57; P 14.55; S 30.05

Found M: 417; 434.9 (cryoscopically in benzene)

Calculated M: 426

SUMMARY

1. For the first time O,O-dialkyl hydrogen phosphorothiolothionates have been prepared in the pure state in the form of liquids that may be vacuum-distilled. Some of their properties have been investigated.

2. It has been shown that the dialkyl hydrogen phosphorodithioates formed by the reaction of alcohols with the two phosphorus sulfides P_4S_7 and P_4S_{10} are identical.

3. It has been shown that, when O,O-dialkyl hydrogen phosphorothiolothionates are oxidized with iodine, the corresponding disulfides are formed.

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* See Consultants Bureau English translation, page 661 ff.

CRYSTALLINE ORGANOLITHIUM COMPOUNDS.

COMPOUNDS OF THE AROMATIC SERIES

T. V. Talalaeva and K. A. Kocheshkov

Although aromatic organolithium compounds have been frequently described in solution (mainly ethereal and containing also appreciable amounts of lithium halides, diaryls, finely divided lithium, etc.), there is only one example in the literature of the isolation of a crystalline aromatic organolithium compound [1], namely phenyllithium:

$$(C_6H_5)_2Hg + 2C_2H_5Li \longrightarrow (C_2H_5)_2Hg + 2C_6H_5Li \qquad (1)$$

Improved and more general methods of preparing pure crystalline compounds are , however, of considerable interest. For carrying out a number of precise, for example physicochemical, investigations relating to complex formation, we required pure crystalline compounds, or pure solutions prepared from these.

The method indicated in Equation 1 suffered from two inherent defects: 1) in the metathetic reaction diethylmercury is formed, and its high toxicity is well known; 2) the preparation of pure ethyllithium is based on the reaction between diethylmercury and lithium. As we had successfully solved the problem of preparing pure crystalline ethyllithium [2], it was necessary to solve also the problem of the replacement in these metathetic reactions of organomercury compounds by other organometallic (or "organoelemental") compounds.

The previously described [3] metathetic reactions between organoelemental compounds and alkyllithiums were not carried out with the object of isolating crystalline organolithium compounds (the presence of these was proved by the formation of carboxylic acids by carbonation of their solutions, the authors' problem being the investigation of the relative strengths of the bonds between the radicals and the various elements. However, as we have shown [2], these metathetic reactions can be widely and successfully applied for the preparation of crystalline organolithium compounds. In this respect different organoelemental compounds are not all of equal value: thus the reactions of RLi with aromatic bromo compounds have the important defect that the secondary condensation reaction II generally occurs:

$$ArBr + RLi \longrightarrow ArLi + RBr; \qquad (I)$$

$$ArLi + RBr \longrightarrow ArR + LiBr \qquad (II)$$

leading to formation of lithium halide, whose solubility in organic solvents is close to that of the aryllithium formed.

In our monograph [4], and also in a paper published in 1951 [2], we emphasized both the undesirability of heating, which accelerates the condensation reaction, and also the necessity for testing for the presence of halide ions in the preparations of aryllithium compounds obtained by this method. Mikhailov and Chernova [5] in their more recent investigations, while applying our methods for the isolation of aryllithium compounds in the bromoarene portion, made no reference to our work and also, unfortunately, did not follow our advice concerning the above-mentioned defects of this reaction.

By applying heating (or by permitting "rapid spontaneous temperature rise" in the preparation of complexes), they created conditions favorable for the condensation reaction and the formation of lithium bromide. Moreover, in the description of the compounds (which they evidently did not isolate, but either used for reaction or decomposed for analysis, directly in the filtration apparatus) there are no indications even of a qualitative test for halide ion. This remark relates particularly to the direct reaction between bromobenzene and lithium. The presence of lithium halide impurity, however, could have greatly affected their results relating to aryllithiums and their etherates (or other complexes), since the possibility of the formation of more complicated compounds was now present.

For example, the well formed crystals that separate from concentrated ethereal solutions of phenyllithium (prepared from bromobenzene and lithium), if analyzed only for lithium (titration with acid), might be taken for the monoetherate or dietherate of phenyllithium. Actually, ternary complexes containing LiBr [6] come down*, and their lithium contents (by titration with acid) happen to be near to those required by the formulas $C_6H_5Li \cdot (C_2H_5)_2O$ and $C_6H_5Li \cdot 2(C_2H_5)_2O$. Mikhailov and Chernova [7], by omitting to detect the presence of lithium bromide in the analysis, came to an incorrect conclusion concerning the formula of their etherate. Incidentally, the authors pass over in silence the fact that the complex nature of uncolored organolithium compounds was first pointed out by us [6].

With regard to the complex nature of colored organolithium compounds, in spite of Mikhailov and Chernova's assertion [7] that the study of the colored and electrically conducting organic compounds of the alkali metals had led them to the "discovery" of the complex nature of substances of this type, we may remark that this fact was already known 25 years ago. In 1926 the complex of triphenylmethyllithium with two molecules of ether (giving good analysis) was isolated [8]; the amine $(C_6H_5)_3CNa \cdot NH_3$ is also known [9]. We cannot believe that Mikhailov and Chernova were not acquainted with the basic original literature on organolithium compounds, but in describing [5] the long known synthesis of the dietherate of triphenylmethyllithium they made no reference to the original source.

We considered that a more expedient route to pure crystalline aryllithium compounds (not containing unavoidable halide impurities) was by the well known metathetic "metal-metal" reaction [3,4]. As compounds of lead (owing to their toxicity) or tin (owing to the sluggishness of the reaction) were inconvenient, we decided to use organoantimony compounds.

For antimony (and correspondingly for bismuth) the reaction is expressed by the following equation:

$$Ar_3Sb + 3C_2H_5Li \longrightarrow 3ArLi + (C_2H_5)_3Sb$$

and the isolation of ArLi is based on the fact that the original aromatic compound Ar_3Sb (or Ar_3Bi) is soluble in benzene and the ethyllithium that reacts with it is also soluble in benzene, whereas of the two products obtained only the aryllithium is precipitated from solution so that it can be isolated in a pure state. The reaction goes under mild conditions (temperature not above 30-40°), relatively slowly, and with a characteristic, often long, induction period.

By this method the following crystalline organolithium compounds of the aromatic series were prepared (from organoantimony compounds): p-tolyllithium (yield 72-82%), o-tolyllithium (62%), m-tolyllithium (48%), phenyllithium (50%), p-bromophenyllithium (quantitative), p-chlorophenyllithium (45.8%), 1-naphthyllithium (46.4%). It is interesting to note that it was not found possible to isolate any phenyllithium when triphenylbismuth was used.

The metathetic reaction with haloarenes (iodo- and bromo-):

$$ArX + C_2H_5Li \longrightarrow ArLi + C_2H_5X$$

is much more rapid (from several seconds to several hours, depending on the radical), even at room temperature. The reaction, unlike those with Ar_3Sb, begins immediately. In all cases analysis was made not only for lithium content, but also for the presence of halide ions. It should be noted that the organolithium compounds obtained always contained some lithium halide impurity, and the amount of this could be fairly considerable when heat was used or the reaction was prolonged.

By this reaction the following compounds were obtained from iodo compounds: o-tolyllithium (53.6%), m-tolyllithium (30%), phenyllithium (52.1%). The following were obtained from bromo compounds: p-tolyllithium (66.0%), phenyllithium (78%), p-bromophenyllithium (76.1%), p-chlorophenyllithium (88.8%), 4-biphenylyllithium (44.4%). The crystalline aromatic organolithium compounds obtained were infusible substances (tests were made in a capillary filled with nitrogen), readily soluble in absolute ether, and insoluble in benzene, hexane, and petroleum ether. In the air p-bromophenyllithium and o-tolyllithium ignited (yellow flame); phenyllithium charred and smoldered. All the compounds reacted with water with a flash and charring.

Large crystals of p-chlorophenyllithium and 1-naphthyllithium became white on the surface when decomposing in the air, but they continued to give the qualitative reaction for ArLi with Michler's ketone. The compounds obtained gave the usual reactions of organolithium compounds (see, for example the reaction of phenyllithium with benzophenone and with stannic chloride, also the color reactions).

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* They are similar, to a certain extent, to the organomagnesium complexes, e.g. $2ArLi \cdot LiBr \cdot 2(C_2H_5)_2O$.

EXPERIMENTAL

Owing to the sensitivity of organolithium compounds to the moisture, carbon dioxide, and oxygen in the air, the work with them was carried out in an atmosphere of pure dry nitrogen. We used nitrogen from cylinders (oxygen content not higher than 0.3%), and purified it by passing it through two furnaces, each 1 meter long, containing copper turnings at 450°, and three columns of the same length containing solid caustic potash, calcium chloride, and phosphoric oxide on glass wool respectively.

The reactions were carried out in apparatus with standard joints (Figures 1 and 2). The upper openings of the vessels (narrow joint A) served for the addition of the solutions and the stirring of the precipitate; also, when necessary, a reflux condenser was attached at this joint. The side tubes of the vessels (wider joint B) served for the connection of the filtration apparatus (Figure 3), and also, sometimes, of a dropping funnel. The joints were lubricated with silicone grease. Before use, the apparatus was carefully dried at 120° and cooled while a current of nitrogen was passing. The three-way tap at the side of the apparatus (C, Figures 1 and 2) permitted connection to the stream of nitrogen, which terminated in a drying system consisting of V-shaped tubes containing phosphoric oxide on glass wool, calcium chloride, and sulfuric acid. The last tube served for the control of the rate at which the nitrogen left. If necessary, 6-8 pieces of apparatus could be connected in series through the tap C. They were connected by means of thick-walled, elastic, red rubber tubing. Such a connection system permitted the apparatus to be maintained under a small pressure of nitrogen, even when the caps at A and B (Figures 1 and 2) were removed for a short time (the reaction mixture was always protected by a stream of nitrogen).

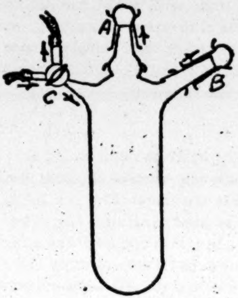

Fig. 1.

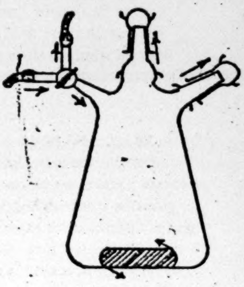

Fig. 2

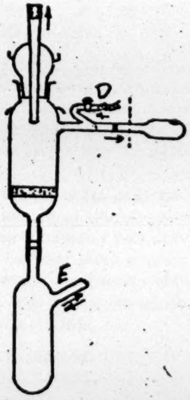

Fig. 3.

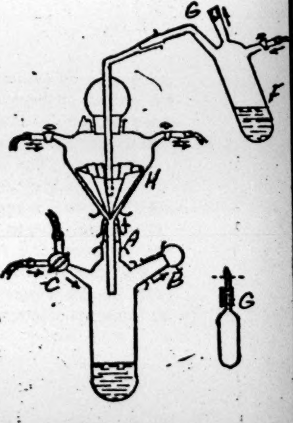

Fig. 4.

The apparatus represented in Fig. 3 was used for filtration. When the substance had been completely transferred to the filter, the first apparatus was disconnected and the upper opening of the filtration apparatus was closed with a stopper. The residue on the filter was washed three or four times with pentane and the receiver for the filtrate E was disconnected, the lower end of the apparatus being connected to the drying system (see above). The apparatus was turned on its side (side tube upwards), and the precipitate was distributed over the whole length of the apparatus by tapping. The precipitate was dried in the nitrogen stream until it could be readily poured out. It is not recommended that the precipitate be dried on the filter by passing nitrogen through it. The dry substance was sealed in tubes, which were connected to the side tube. The tubes were previously filled with nitrogen (otherwise charring and decomposition might occur).

The dissolution of ethyllithium in benzene was carried out in the vessel F (Fig. 4). Very often, particularly when large amounts (3-4 g) of ethyllithium were taken, turbid solutions were obtained; they were filtered in the apparatus H through an ordinary folded filter paper previously dried over phosphoric oxide. The direction of the nitrogen stream is indicated by arrows in all the diagrams. Vessels of various dimensions were taken; the reaction vessels (Figures 1 and 2) had volumes from 15 to 500 ml, and the volume of the filtration apparatus varied correspondingly (Figures 3 and 4). All the solvents must be pure and dry (thiophene-free benzene).

Preparation of p-Tolyllithium

a) From Tri-p-tolylantimony [11]. In an apparatus provided with a magnetic stirrer (Fig. 2) 82 ml of a solution of ethyllithium (1.61 g, i.e. 0.042 mole) in benzene was placed, and 10 ml of a hot (35-40°) benzene solution of tri-p-tolylantimony (3.9 g, i.e. 0.01 mole) was added. There was no noticeable reaction. The mixture was stirred for six hours at 18-20°, and then for 14 hours at 30-35°. At the end of this period a sharp increase in the turbidity of the solution was to be observed, and after 5-10 minutes the solution became quite opaque owing to the presence of a fine white precipitate of p-tolyllithium. Stirring was continued at 30-35° for a further 40 hours. The filtration apparatus (Fig. 3) was then attached in a stream of nitrogen to the side tube; nitrogen was passed for five minutes, and filtration was then effected under a pressure of nitrogen. The very fine white precipitate was very readily transferred to the filter; it was washed on the filter with pentane (four portions of 15 ml), dried in a stream of nitrogen at 35-40° for one hour, and sealed in tubes. The yield was 72-82%, calculated on the tri-p-tolylantimony taken. The reaction may be carried out in the apparatus shown in Fig. 1, without stirring. The yield is of the same order, but larger crystals are obtained.

Found %: Li 7.26 ; 7.28
C_7H_7Li Calculated %: Li 7.08

When p-tolyllithium crystals are poured out in the air, they do not ignite spontaneously; on coming into contact with water or alcohol, they decompose with a strong hissing noise accompanied by charring and sometimes by a yellow burst of flame. P-Tolyllithium is infusible, and is readily soluble in ether, but poorly soluble in benzene and hexane; it gives the usual color reaction with Michler's ketone. When this test is done with p-tolyllithium in benzene solution, it is necessary to heat the mixture to the boil (owing to the poor solubility of the lithium compound in benzene).

b) From Tri-p-tolylbismuth. In the apparatus shown in Fig. 1, 15 ml of a benzene solution of ethyllithium (0.69 g, i.e. 0.019 mole) was placed, and a solution of 2.4 g (0.005 mole) of tri-p-tolylbismuth [12] in 5 ml of benzene was added. When the solutions were mixed, a very slight yellowing was observed. The reaction mixture was set aside at room temperature, and after about a month the formation of isolated large clear crystals was to be observed on the sides of the vessel; the quantity of these gradually increased. They were then filtered off from the solution, washed twice with pentane (10 ml each time), dried, and sealed in tubes. The yellowish crystals obtained weighed 0.965 g (66.1%).

Found %: Li 7.09; 7.03
C_7H_7Li Calculated %: Li 7.08

c) From p-Bromotoluene. p-Bromotoluene (1.7 g, i.e. 0.01 mole) dissolved in 5 ml of benzene was added to 0.36 g (0.01 mole) of ethyllithium in 15 ml of benzene. No changes occurred when the solutions were mixed. After one day, characteristic large crystals of p-tolyllithium, together with a small amount of fine precipitate, separated. The usual treatment yielded 0.64 g (66 %) of p-tolyllithium containing some lithium bromide as impurity.

Found %: Li 6.31; 6.32
C_7H_7Li. Calculated %: Li 7.08

Preparation of o-Tolyllithium

a) From Tri-o-tolylantimony. From 15 ml of a benzene solution of ethyllithium (0.69 g, i.e. 0.019 mole) and 1.97 g (0.005 mole) of tri-o-tolylantimony in 10 ml of benzene, treated under the usual conditions (see above), a fine precipitate of o-tolyllithium (0.9 g, 62%) was obtained after the mixture had been allowed to stand at room temperature for two weeks.

Found %: Li 6.95; 6.87

C_7H_7Li **Calculated %:** Li 7.08

b) From o-Iodotoluene. From 0.36 g (0.01 mole) of ethyllithium in 16 ml of benzene and 2.17 g (0.01 mole) of o-iodotoluene in 10 ml of benzene, a very fine voluminous white precipitate was obtained (after mixing there was a slight rise in temperature). After standing for 30 minutes, the precipitate was filtered off (it filtered very slowly), and was washed as usual with pentane and dried. A positive test for halide was obtained. The yield of o-tolyllithium was 0.62 g (53.6%).

Found %: Li 7.37; 7.12

C_7H_7Li **Calculated %:** Li 7.08

Preparation of m-Tolyllithium

a) From Tri-m-tolylantimony. A benzene solution (15 ml) containing 0.69 g (0.019 mole) of ethyllithium and 1.97 g (0.005 mole) of tri-m-tolylantimony in 15 ml of benzene were taken. The solution was set aside for two weeks at room temperature, and after the usual treatment it yielded 0.7 g (48%) of m-tolyllithium in the form of a finely crystalline white precipitate.

Found %: Li 6.92; 6.81

C_7H_7Li. **Calculated %:** Li 7.08

b) From m-Iodotoluene. The substances taken were ethyllithium (0.36 g, i.e. 0.01 mole) in 17 ml benzene and m-iodotoluene (2.17 g, i.e. 0.01 mole) in 10 ml of benzene. Mixing was accompanied by slight turbidity, and the mixture, after standing for two days, yielded 0.29 g (30%) of m-tolyllithium in the form of a fine yellowish powder. In the air the substance darkened and smoldered; it reacted with alcohol with a burst of yellow flame. A positive test for halide was obtained.

Found %: Li 6.73; 6.70

C_7H_7Li **Calculated %:** Li 7.08

Preparation of Phenyllithium

a) From Triphenylantimony. Triphenylantimony (2.25 g, i.e. 0.007 mole) in 15 ml of benzene was added to ethyllithium (0.75 g, i.e. 0.021 mole) in 15 ml of benzene. After a three-hour heating at a gentle boil (the liquid yellowed slightly), the separation of white needles suddenly began. The amount of these quickly increased, and after 10-15 minutes they filled the whole of the solution. Heating was continued for two hours, and was followed by cooling to room temperature, filtration, four washes with pentane and drying. The yield was 0.8 g (50%).

In another experiment (2.3 g of ethyllithium, 5 g of triphenylantimony, in 50 ml of benzene, under the same conditions) separation of crystals was observed already after 30 minutes. The yield of phenyllithium was 2.23 g (41%).

Found %: Li 8.28; 8.09

C_6H_5Li. **Calculated %:** Li 8.27

Phenyllithium forms infusible white needles. On coming into contact with air, it smolders, without igniting (the spontaneous inflammability of phenyllithium, described in the literature, must be ascribed to the presence of ethyllithium as impurity). When put into water, phenyllithium decomposes with much hissing and bursts of flame (yellowish). It is of poor solubility in benzene and petroleum ether, and readily soluble in absolute ether.

b) From Iodobenzene. When solutions, previously cooled to + 5° of 0.36 g (0.01 mole) of ethyllithium in 17 ml of benzene and of 2 g (0.01 mole) of iodobenzene in 10 ml of benzene were mixed, there was a slight evolution of heat and the whole mass solidified (the behavior is similar to that which we have observed when a benzene solution of butyllithium acts upon diphenylmercury). A small amount of isopentene was added, and the precipitate was rubbed out with a rod and filtered off. It was washed three times with pentane (15 ml each time), and dried at 35-40°. The yield of phenyllithium, in the form of a fine powder, was 0.44 g (52.1%). A positive test for halide was obtained.

Found %: Li 7.95; 8.00
C_6H_5Li Calculated %: Li 8.27

c) From Bromobenzene. When 0.36 g (0.01 mole) of ethyllithium in 15 ml of benzene was mixed with 1.56 g (0.01 mole) of bromobenzene in 5 ml of benzene and the mixture was allowed to stand for two hours, a slight turbidity appeared which gradually increased in intensity. After one day characteristic crystals of phenyllithium had separated. A further day was allowed for completion of the reaction, and the usual treatment followed, giving 0.65 g (78%) of phenyllithium. The substance contained lithium bromide as impurity. It should be noted that when the reaction mixture containing the crystals of phenyllithium was allowed to stand for a longer period (more than a month), a gradual disappearance of the characteristic crystalline precipitate was observed, and the separation of a small amount of a more compact fine white precipitate of lithium bromide occurred (as a result of the condensation reaction).

Found %: Li 6.97; 7.03
C_6H_5Li Calculated %: Li 8.27

Preparation of Tetraphenyltin. Absolute ether (40ml) was introduced under nitrogen into a round-bottomed four-necked flask fitted with dropping funnel, reflux condenser, tube for the passage of nitrogen, and mercury-sealed stirrer. Crystalline phenyllithium (1.57 g) was dissolved in the ether, and with stirring and external ice cooling stannic bromide (2 g) in dry benzene (10 ml) was added. Before the last portion of the stannic bromide solution had been added, a test with Michler's ketone was positive; after the addition, it was negative. The mixture was boiled gently with stirring for two hours. The usual treatment yielded 1.58 g (79%) of tetraphenyltin, m.p. 224-225°. In the residue from the separation of $(C_6H_5)_4Sn$, a test with an alcoholic solution of silver nitrate gave considerable blackening, indicating the presence of hexaphenyldistannane.

Preparation of Triphenylmethanol. The preparation was carried out in the same apparatus. Absolute ether (25 ml) was poured in, and then a tube of crystalline phenyllithium (0.35 g, i.e. 1 mole) was opened and its contents were sprinkled in through the side tube of the flask in a counter current of nitrogen. The crystals dissolved immediately. Benzophenone (0.76 g, i.e. 1 mole) was dissolved in absolute ether (20 ml), and the solution was added, the course of the being checked by qualitative tests with Michler's ketone for the presence of phenyllithium. The amount added before the test became negative was 18 ml, i.e. 0.72 g of benzophenone. The reaction mixture was stirred further for an hour at room temperature, and the usual treatment then yielded 0.65 g of slightly greyish crystals (70% calculated on the amount of benzophenone taken for reaction). The melting point after recrystallization from alcohol was 162°.

Preparation of p-Bromophenyllithium

a) From Tri-p-bromophenylantimony. A warm solution of 2.9 g (0.005 mole) of tri-p-bromophenylantimony in 15 ml of benzene (it was necessary to warm for complete solution) was added under nitrogen to 30 ml of a benzene solution of ethyllithium (0.79 g, i.e. 0.022 mole). Some yellowing and clouding was observed when the solutions were mixed. The solution was allowed to stand at room temperature. After 30 minutes the turbidity had appreciably increased, and after an hour the solution was completely opaque and was full of a white suspension that gradually settled. After 12 hours from the start of the reaction, the reaction vessel was about two-thirds full of white precipitate, above which was a clear, almost colorless solution. The precipitate was filtered off, washed with two 15 ml portions of pentane, and dried in a current of nitrogen at 40-45° for one hour. The very fine white powder obtained was sealed in tubes. The yield was quantitative.

Found %: Li 4.15; 4.16
BrC_6H_4Li Calculated %: Li 4.28

In the air, p-bromophenyllithium immediately ignites with a yellow flame. The bursts of flame are similar (intensity) to those given by ethyllithium. A few crystals introduced under nitrogen into a benzene solution of Michler's ketone and treated in the usual way give an intense green coloration.

b) From p-Dibromobenzene. The solutions taken were: 0.18 g (0.005 mole) of ethyllithium in 10 ml of benzene, and 1.17 g (0.005 mole) of p-dibromobenzene in 5 ml of benzene. As soon as the solutions were mixed, a strong turbidity appeared, and after one hour a considerable amount of precipitate had separated. The mixture was allowed to stand for six hours, and after the usual treatment 0.61 g (76.1%) of p-bromophenyllithium was isolated. A positive test for halide was obtained.

Found %: Li 4.91; 4.65
BrC_6H_4Li Calculated %: Li 4.28

Preparation of p-Chlorophenyllithium

a) From tri-p-chlorophenylantimony. A solution of 2.28 g (0.005 mole) of tri-p-chlorophenylantimony in 10 ml of benzene was added to 30 ml of a solution of ethyllithium (0.79 g, i.e. 0.022 mole); slight yellowing occurred. The solution was allowed to stand at 18-20°. After about one hour some fine white crystals had appeared on the bottom of the vessel, and after three days the amount of crystals had reached its maximum. The solution was then filtered under nitrogen and the precipitate was washed with benzene and pentane and dried in a current of nitrogen for 30 minutes at 35-45°, yielding 0.8 g (45.8%) of p-chlorophenyllithium.

Found %: Li 5.64; 5.82

ClC_6H_4Li Calculated %: Li 5.86

The substance does not burn in the air, but slowly turns white. A crystal that has lain in the air for about two minutes and has becomewhite at the surface will still give an intensive green coloration when heated with a benzene solution of Michler's ketone and given the usual treatment.

b) From p-bromochlorobenzene. The solutions taken were 0.36 g (0.01 mole) of ethyllithium in 17 ml of benzene and 1.91 g (0.01 mole) of p-bromochlorobenzene in 5 ml of benzene. No changes occurred when the solutions were mixed. After one day large yellowish crystals (1.05 g, 88.8%) of p-chlorophenyllithium separated.

Found, %: Li 5.69; 5.62

ClC_6H_4Li Calculated %: Li 5.86

Preparation of 1-Naphthyllithium from Tri-1-naphthylantimony

A suspension of 3.9 g (0.01 mole) of tri-1-naphthylantimony [13] in 15 ml of hot benzene was added to 75 ml of a benzene solution of 1.47 g (0.042 mole) of ethyllithium. The mixture was heated in a water bath at 70-75°, and after about five minutes the tri-1-naphthylantimony went completely into solution. The solution became slightly yellow, and after one hour of heating a turbidity appeared, which quickly turned in a precipitate (small). Heating was continued further for five hours, and no increase in the amount of precipitate was observed. The reaction mixture was set aside at room temperature for ten days: Fine dark-colored crystals were to be observed on the walls of the vessel. The solution was filtered and the crystals were washed three times with pentane, dried, and sealed in tubes. The yield of 1-naphthyllithium was 2.18 g (56.4%).

Found %: Li 5.26; 5.10

$C_{10}H_7Li$ Calculated %: Li 5.18

1-Napthyllithium does not burn in the air. It reacts with water with charring and intense hissing (sometimes accompanied by yellow bursts of flame). It is soluble in absolute ether, and it gives an intense coloration in the Michler's ketone test.

Preparation of 4-Biphenylyllithium from 4-Bromobiphenyl

The solutions taken were 0.18 g (0.005 mole) of ethyllithium in 10 ml of pure benzene and 1.16 g (0.005 mole) of 4-bromobiphenyl in 5 ml of benzene. No changes occurred when the solutions were mixed. After standing for two days, the solution was found to be full of large white matte crystals which formed clusters. The crystals were filtered off, washed with two 10 ml portions of pentane, and dried at 30-35°. The product was 0.35 g (44.4%) of 4-biphenylyllithium in the form of a fine white powder. It contained lithium bromide as impurity.

Found %: Li 3.91; 3.98

$C_{12}H_9Li$. Calculated %: Li 4.33

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SYNTHESIS AND PROPERTIES OF ORGANOSILICON ESTERS OF MONO- AND DI-BASIC ACIDS

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Only four trialkylsilyl esters (acyloxytrialkylsilanes, $R_3SiOOCR'$) are known. They are all acetic acid derivatives, the alcohol residues being trimethylsilyl [1, 2, 3], triethylsilyl [4], tripropylsilyl [5], and triphenylsilyl [6]. They were prepared by the action of acetic anhydride on $R_3SiOC_2H_5$, or of sodium acetate on R_3SiCl. Organosilicon esters of dibasic and higher monobasic acids have not been described in the literature.

With the object of studying the properties of organosilicon esters, we have now undertaken the synthesis of five esters of dibasic acids and three esters of higher monobasic acids. For these syntheses we chose the method, which has not been used previously, of direct reaction of the acids with R_3SiCl to give esters of the types $R_3SiOOCR'$ and $R_3SiOOC(CH_2)_x$ $COOS_1R_3$:

$$R_3SiCl + HOOCR' \rightarrow R_3SiOOCR' + HCl ;$$
$$2R_3SiCl + HOOC(CH_2)_xCOOH \rightarrow R_3SiOOC(CH_2)_xCOOSiR_3 + 2HCl.$$

The reaction was carried out by heating a mixture of the components in a flask fitted with reflux condenser and protected by a P_2O_5 column from the action of atmospheric moisture.

All the esters obtained were clear colorless mobile liquids having a feeble characteristic odor, somewhat reminiscent of mold. In their tendency to undergo hydrolysis, the synthesized esters differed notably from their analogs, the organic esters: They were all readily hydrolyzed by dilute solutions of sodium and potassium carbonates. The hydrolysis of certain organosilicon esters of dibasic acids occurred rapidly, even under the influence of atmospheric moisture, as was readily revealed by the formation of a precipitate of the solid acid. Owing to this, it was not found possible in certain cases to determine the specific gravity of the ester.

Of the five esters of dibasic acids that were synthesized, the trimethylsilyl ester of azelaic acid and the triethylsilyl ester of succinic acid were hydrolyzed exceptionally readily, being almost completely decomposed in the air in the course of 60-90 minutes. The trimethylsilyl ester of adipic acid was somewhat more stable, appreciable hydrolysis being observed only after 15-18 hours. The most stable were the triethylsilyl esters of adipic and azelaic acids. Incipient hydrolysis of the latter was to be observed only after 24 hours, and appreciable hydrolysis of the first ester was to be observed only after 1.5-2 days, even when an addition of water was made.

It would be premature on the basis of these few observations to form any definite conclusions concerning the effect of the molecular weights of the acids and of the hydrocarbon radicals attached to the silicon on the stability to hydrolysis of organosilicon esters. It may be noted only that, in the case of the adipic and azelaic esters studied, the replacement of trimethylsilyl by triethylsilyl increases the stability of the esters to hydrolysis. Owing to the impossibility of using treatments with solutions of sodium or potassium carbonate, the isolation of the esters in the pure state was attained by repeated fractionation at low pressure in a current of dry air. In certain cases elimination of the residual acid was effected by freezing this out in petroleum ether solution. The physiochemical constants of the esters are given in the table.

In absence of an accepted nomenclature for organosilicon esters, the synthesized compounds were named by analogy with the corresponding organic compounds.

EXPERIMENTAL

I. Triethylsilyl Butyrate

a) A mixture of 20 g (0.13 mole) of chlorotriethylsilane and 52 g (0.59 mole) of butyric acid was heated for 85 hours. Two vacuum fractionations yielded 14 g (0.07 mole) of the ester as a colorless mobile liquid. The yield was 52 %.

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	MR Found	MR Calc. *
1	$(C_2H_5)_3SiOOC_3H_7$	85-87	10	1.4250	0.8850	58.46	58.82
		83.5-85 **	9	1.4245	0.8851	58.39	58.82
2	$(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH(CH_3)_2$	92.5-93.5	10	1.4258	—	—	—
3	$(C_2H_5)_3SiOOC \cdot C_6H_{13}$	127.5-129	1	1.4303	—	—	—
4	$[(C_2H_5)_3SiOOC \cdot CH_2]_2$	172.5	10.5	1.4450	0.9518	96.90	96.99
5	$[(CH_3)_3SiOOC \cdot CH_2 \cdot CH_2]_2$	153-154	24.5	1.4275	0.9589	77.84	78.47
6	$[(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH_2]_2$	221-222	26	1.4475	0.9496	105.50	106.25
7	$[(CH_3)_3SiOOC \cdot CH_2 \cdot CH_2 \cdot CH_2]_2CH_2$	180-181	23	1.4310	—	—	—
8	$[(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH_2 \cdot CH_2]_2CH_2$	240-241	22	1.4500	0.9438	118.65	120.14

* MR calculated by E. Warrick's method [8].

** The ester was prepared from sodium butyrate.

Found %: Si 13.89 *; 13.92

$C_{10}H_{22}SiO_2$. Calculated %: Si 13.86

Found ester value **: 263.0; 261.0

$C_{10}H_{22}SiO_2$. Calculated ester value: 277.2

b) A mixture of 37 g (0.25 mole) of chlorotriethylsilane, 93 g (0.75 mole) of dry potassium butyrate, and 300 ml of dry toluene was heated at the boil for 26 hours. The toluene layer was removed from the precipitate by filtration, and the precipitate was washed with a fresh portion of dry toluene, which was then united with the main filtrate. After the toluene had been distilled off, the residue was vacuum-fractionated twice. Two fractions were separated. The yield of ester (the two fractions being treated together for calculation) was 90%.

Fraction I. b.p. 80-81° / 10 mm; 18 g

Fraction II. b.p. 83.5-85°/ 9 mm; 27 g

Analysis of Fraction I:

Found %: Si 12.88; 12.96

Analysis of Fraction II:

Found %: Si 13.57; 13.53

$C_{10}H_{22}SiO_2$. Calculated %: Si 13.86

II. Triethylsilyl Isovalerate

A mixture of 19 g (0.12 mole) of chlorotriethylsilane and 13 g (0.12 mole) of isovaleric acid was heated for 40 hours. Unchanged acid was distilled off, and the residue was treated in the cold with a 10% solution of sodium carbonate and with water, and was dried with anhydrous Na_2SO_4. Two vacuum fractionations yielded a fraction of b.p. 92.5-93.5°/10 mm. The yield was 26%.

Found %: Si 12.58

$C_{11}H_{24}SiO_2$. Calculated %: Si 12.97

Found ester value: 251.0, 243.0

$C_{11}H_{24}SiO_2$. Calculated ester value: 259.3

III. Triethylsilyl Heptanoate

A mixture of 19 g (0.12 mole) of chlorotriethylsilane and 16 g (0.12 mole) of heptanoic acid was heated for 40 hours. The whole of the reaction product was treated with a solution of sodium carbonate, washed with water, and dried with Na_2SO_4. Fractionation yielded 9 g of triethylsilanol (b.p. 157-158°; n_D^{20} 1.4300), 3 g of hexaethyldisiloxane (b.p. 222-233°) and 2 g of a fraction of b.p. 127.5-129°/7 mm.

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* Silicon was determined by mineralization of a weighed amount by heating with a mixture of concentrated sulfuric and nitric acids.

** The ester value was determined by hydrolysis of a weighed amount with solutions of alkali in diethylene glycol [7].

Analysis of fraction of b.p. 127.5-129°

Found %: Si 9.59; 9.45

$C_{13}H_{28}SiO_2$. Calculated %: Si 11.48

Found ester value: 230.0; 236.0

$C_{13}H_{28}SiO_2$. Calculated ester value: 229.5

IV. Bis(triethylsilyl) Succinate

A mixture of 50 g (0.33 mole) of chlorotriethylsilane and 12 g (0.10 mole) of succinic acid was heated for 107 hours. A semiliquid dark-colored mass formed in the flask. Unchanged acid was removed by filtration through a funnel fitted with a porous plate, and the filtrate was vacuum-fractionated. All the fractions separated contained crystalline acid as impurity. In order to remove this impurity, the main fraction, b.p. 192-195°/18 mm, was washed three times with a 10% solution of sodium carbonate and then with water; it was dried over Na_2SO_4. Repeated fractionation under reduced pressure yielded triethylsilanol (b.p. 54°/10.5 mm; n_D^{19} 1.4330; found Si 21.43%; calculated Si 21.10%) succinic acid (b.p. 180°; the literature gives 183°) formed by hydrolysis of the ester, and a small amount of a fraction of b.p. 172.5°/10.5 mm.

Ester value of fraction of b.p. 172.5°:

Found: 309.5; 310.5

$C_{16}H_{34}Si_2O_4$. Calculated: 323.7

V. Bis(trimethylsilyl) Adipate

A mixture of 46 g (0.42 mole) of chlorotrimethylsilane and 25 g (0.17 mole) of adipic acid was heated for 60 hours. Unchanged acid was filtered off with exclusion of moisture, and the filtrate was fractionated in a current of dry air. A fraction was isolated (b.p. 144.5-146°/19 mm) containing a small amount of crystalline acid as impurity. In order to remove this, the fraction was diluted with an equal volume of petroleum ether and cooled to −15°, and the precipitate of acid formed was filtered off at this temperature through a porous glass filter No. 3, with exclusion of moisture. When the petroleum ether was distilled off, it was accompanied by the last traces of solid acid, and 14 g (28%) of ester, b.p. 153-154°/24.5 mm, was obtained.

Found %: Si 17.60; 17.95

$C_{12}H_{26}Si_2O_4$. Calculated %: Si 19.20

The analysis results indicate a low silicon content. This may be explained by the partial evaporation of trimethylsilanol (b.p. 100°) formed by decomposition of the ester during heating with the mixture of H_2SO_4 and HNO_3.

Found ester value: 394.0; 397.0

$C_{12}H_{26}Si_2O_4$. Calculated ester value: 385.6

VI. Bis(triethylsilyl) Adipate

A mixture of 50 g (0.33 mole) of chlorotriethylsilane and 30 g (0.2 mole) of adipic acid was heated for 30 hours. The ester was isolated in the manner described for the preceding experiment. The ester boiled at 221-222°/26 mm.

Found %: Si 14.77

$C_{18}H_{38}Si_2O_4$. Calculated %: Si 14.97

Found ester value: 300.5; 308.0

$C_{18}H_{38}Si_2O_4$. Calculated ester value: 299.4

VII. Bis(trimethylsilyl) Azelaate

A mixture of 65 g (0.6 mole) of chlorotrimethylsilane and 38 g (0.2 mole) of azelaic acid was heated for 92 hours. As a result of treatment similar to that used in the two preceding experiments, an ester of b.p. 180-181°/23 mm was isolated.

Found %: Si 16.0

$C_{15}H_{32}Si_2O_4$. Calculated %: Si 16.84

Found ester value: 347.0

$C_{15}H_{32}Si_2O_4$. Calculated ester value: 336.3

VIII. Bis(triethylsilyl) Azelaate

A mixture of 45 g (0.3 mole) of chlorotriethylsilane and 20 g (0.11 mole) of azelaic acid was heated for 54 hours. After three fractionations at reduced pressure and freezing out under conditions used in previous experiments, 25 g (54%) of ester, b.p. 240-241°/22 mm, was isolated.

Found %: Si 12.76; 12.67
$C_{21}H_{44}Si_2O_4$. Calculated %: Si 13.43
Found ester value: 282.0; 286.0
$C_{21}H_{44}Si_2O_4$. Calculated ester value: 269.2

SUMMARY

1. By direct reaction of trialkylchlorosilanes with saturated mono- and di-basic acids the syntheses have been effected of eight organosilicon esters that have not been described previously in the literature; they include five representatives of the completely unstudied class of esters of dibasic acids.

2. It has been established that most of the synthesized esters are readily hydrolyzed, even by the moisture of the air, a particularly marked tendency to undergo hydrolysis being possessed by esters containing trimethylsilyl radicals.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 51. INVESTIGATION OF THE POLYESTER EXCHANGE REACTION BY THE USE OF DEUTERIUM

D. N. Kursanov, V. V. Korshak and S. V. Vinogradova

As one of us in conjunction with other investigators has established [1], the process of polycondensation cannot be completely described solely in terms of reactions between terminal functional groups. In addition to these reactions which lead to chain growth, others, mainly of a degradational character, occur, these being associated with the presence in the polycondensation products of bonds that may be readily broken under the influence of the starting substances and of other substances of similar chemical nature. In the case of polyesterification, such degradational reactions include acidolysis and glycolysis [2], alcoholysis [3], and transesterification at the expense of ester linkages [4]. In the case of polyamides, such degradational reactions must be considered to include acidolysis [5, 6], aminolysis [6], and transamidation [7].

The acidolysis reaction of a polyester has been investigated by one of us in conjunction with Golubev [2], the example taken being the reaction of polyethylene adipate with adipic acid. It was found that the degree of degradation was directly proportional to the amount of acid taken for acidolysis. A similar picture was observed previously by one of us in conjunction with Rafikov [5] and Zamyatina [6] in investigations of the acidolysis of polyhexamethyleneadipamide by adipic acid.

The alcoholysis of a polyester was investigated by one of us and Golubev, the example taken being the reaction of polyethylene adipate with ethylene glycol; a lowering of the molecular weight of the polyester was found to occur [2]. The laws of the alcoholysis reaction were established particularly clearly by Korshak and Vinogradova for the alcoholysis of polyhexamethylene sebacate in presence of hexadecyl alcohol [3]. Flory [8] examined the alcoholysis of two polyesters differing in molecular weight and having terminal hydroxyl groups He found that in this case also lowering of the molecular weight of the mixture occurred.

The kinetics of the acidolysis and alcoholysis reactions were investigated by two of us with the aid of model reactions of a similar type in which low-molecular-weight substances [9,10] were used. Acidolysis was investigated for ethyl stearate in acetic acid [9], and it was found that at 250° about 44% of the ethyl stearate taken underwent acidolysis. The alcoholysis of ethyl stearate with hexadecyl alcohol (and also the acidolysis reaction) is greatly accelerated by rise in temperature, and at 183° equilibrium is established when 61.5% of the original ethyl stearate has been converted into hexadecyl stearate [10]. In the alcoholysis reaction the process is greatly accelerated by acids, alkalis, and certain metal salts, whereas alcoholysis is only slightly accelerated by addition of acids [9,10].

Apart however from such exchange reactions, in which the end-groups take part, it is possible also for different polymer molecules to react with one another at ester, amide, and other sufficiently polar links [11]. Such reactions must also be degradational, and their role in the general balance of the polycondensation process may evidently be a very important one [12]. However, nobody has yet succeeded in proving the presence of such side reactions experimentally, and any discussion of their significance in the general process must therefore be tentative. The suggestion that such reactions are of considerable importance was made by one of us a considerable time ago [13]. A kinetic investigation of an exchange reaction of this type was carried out by two of us [14]. It was found that the reaction investigated, the transesterification of ethyl stearate and hexadecyl acetate, is greatly accelerated in precence of acid catalysts; alkaline catalysts are somewhat less active. The reaction may occur also in absence of catalyst, but the percent conversion is then considerably lower: Thus in six hours at 183° the degree of conversion was 545 % in presence of sulfuric acid, but only 13.5% in absence of catalyst.

The present investigation was carried out with the object of obtaining direct experimental proof of the occurrence of exchange (transesterification) reactions proceeding at ester groupings in the course of the polycondensation process. We decided to adopt a new method for this purpose; it consisted in the use of compounds containing a labeled atom, namely deuterium. For our labeled compound we chose diethyl succinate-2,3-d_4, which we caused to react with polyhexamethylene sebacate. Investigation of the products of this reaction could be expected to give an unequivocal answer to the question of whether or not there was any interaction involving ester linkages, between the two esters. If the polyester isolated after the reaction with diethyl succinate-2,3-$\underline{d}_2$ were found to contain deuterium, it could be regarded as proved tha, an exchange reaction had occurred in accordance with the following equation:

$$\begin{array}{rcl} -O(CH_2)_6OOC(CH_2)_8CO & \vdots & O(CH_2)_6OOC(CH_2)_8CO- \\ & & + \\ C_2H_5O & \vdots & OCCHDCHDCOOC_2H_5 \quad \rightarrow \end{array}$$

$$\rightarrow -O(CH_2)_6OOC(CH_2)_8COOC_2H_5 + C_2H_5OOCCHDCHDCOO(CH_2)_6OOC(CH_2)_8CO-$$

It would be necessary, however, to make sure that unchanged diethyl succinate-2,3-$\underline{d}_2$ was completely removed from the polyester, for only then would the answer obtained to our question be unequivocal. On this account a special procedure was evolved for the purification of the polyester, and this ensured that it was almost completely freed from diethyl succinate-2,-$\underline{d}_2$. .

EXPERIMENTAL

Starting Materials

Diethyl Succinate-2,3-$\underline{d}_2$. Diethyl succinate-2,3-$\underline{d}_2$ was prepared by hydrogenation of diethyl maleate in ethyl acetate solution with deuterium-enriched hydrogen in presence of a palladium catalyst. The heavy hydrogen required was obtained by electrolysis of an alkaline solution of deuterium oxide in water. A solution of caustic soda (1.2 g) in distilled water (2 ml) was placed in a U-shaped electrolysis vessel, and 2 ml of deuterium oxide was added. A current of not greater than 0.5 amp was used. The deuterium-rich hydrogen obtained was collected in a gas holder which was filled with a dilute solution of copper sulfate in distilled water (the solution was pale blue).

Diethyl maleate (10.6g) and ethyl acetate (15 ml) were introduced into a hydrogenation flask, and about 1 ml of a palladium catalyst, prepared by a well known method [15], was added. The air in the flask was displaced with ordinary hydrogen, and the flask was then connected with the gas holder containing deuterium-rich hydrogen. A Drechsel vessel containing sodium plumbite was placed between the gas holder and the flask. The flask was shaken mechanically during the hydrogenation, which was continued until absorption of the hydrogen had completely stopped (about five hours). The total amount of hydrogen absorbed was about 1.5 liters, which was only slightly greater than the amount theoretically required. When absorption of hydrogen had stopped, the catalyst was filtered off and washed with a little fresh ethyl acetate; the filtrate was vacuum-distilled, the fraction boiling at 94-95°/6mm being collected. The product was 15 g (94.6%) of diethyl succinate-2,3-$\underline{d}_2$. The deuterium content of the ester was determined by burning it and measuring the density of the resulting water by the float method. The density excess of the water was found to be 3000 γ, which corresponds to a 21% deuterium content in the diethyl succinate-2,3-$\underline{d}_2$ obtained; hydrogen, for this purpose, being treated as one C-H bond formed in the hydrogenation process.

Polyhexamethylene Sebacate. 1,6-Hexanediol (10g) and sebacic acid (20.54 g, a 20% excess) were placed in a condensation tube and heated in a current of nitrogen, previously purified from oxygen. The temperature was gradually raised: the first seven hours at 180°, after which the temperature was raised to 256° in the course of nine hours. A vacuum of 2-3 mm was applied, and the reaction mixture was maintained at this same temperature for 35 hours. In order to purify the polyester obtained, it was dissolved in benzene, and, after filtration of the solution, precipitated with petroleum ether. The polyhexamethylene sebacate obtained had a molecular weight, determined from its viscosity in benzene solution, of 3400. End-group determinations showed that all the end groups were carboxyls.

Method of Investigation and Results

A very important question, which had to be settled before proceeding to the main investigation, was the possibility of completely removing diethyl succinate-2,3-$\underline{d}_2$ from the polyester after the reaction. It was essential to be absolutely sure that the whole of the unchanged diethyl succinate-2,3-$\underline{d}_2$ could be removed from the polyester, and that the polyester would not retain any in the adsorbed state. Only then could we draw any conclusions on the basis of determinations of deuterium content of the polyester after its reaction with the low-molecular-weight ester.

With this object a weighed amount of the polyester was melted and mixed with a weighed amount of diethyl succinate-2,3-$\underline{d}_2$. The homogeneous mixture obtained was subjected to various treatments in order to remove diethyl succinate-2 3-$\underline{d}_2$, and the polyester, purified in one way or another, was carefully dried. It was then burnt, and the resulting water was collected and its density excess was determined.

The possibility of effecting purification by repeated extraction of the polyester with ether was tried : A mixture obtained from 1.75 g of polyester and 0.54 g of diethyl succinate-2,3-$\underline{d}_2$ was washed repeatedly with ether and was then left overnight under a layer of ether. On the next day the polyester was filtered off, dried and burned. The density excess of the water obtained was 360γ ; this method of purification was therefore ineffective. Purification by reprecipitation of the polyester was found to be more effective: a mixture obtained from 2g of polyester and 0.8 g of diethyl succinate-2,3-$\underline{d}_2$ was dissolved in benzene and precipitated with petroleum ether, the operation being repeated five times (in experiments in which only three precipitations were given, the density excess of the combustion water was 45γ); the polyester was then repeatedly shaken with ether over a period of three days, and was then filtered off and burned. The density excess of the combustion water was 30γ, i.e. in this case practically complete purification of the polyester from diethyl succinate-2,3-$\underline{d}_2$ had been effected. This purification technic was applied by us in the isolation of the polyester after reaction with diethyl succinate-2,3-$\underline{d}_2$. It should be noted that these experiments have indicated how tenaciously low-molecular-weight impurities may be held in macromolecular compounds and have shown that extraction is a completely unreliable method for the removal of such impurities.

Experiments on the exchange reaction of polyhexamethylene sebacate with diethyl succinate-2,3-$\underline{d}_2$ were carried out as follows: polyhexamethylene sebacate (4.02 g) and diethyl succinate-2,3-$\underline{d}_2$ (2.46 g) 1 mole per basal mole (per unit link) of polyester, $[-O(CH_2)_6OOC(CH_2)_8CO-]$ were placed in an ampoule, which was freed from air by repeated blowing with nitrogen followed by evacuation. The ampoule was then sealed off and placed in the vapors of boiling biphenyl (b.p. 250°). Heating was continued for ten hours. The reaction product was purified by the five-fold precipitation method already described, and was then burned. The density excess of the combustion water was found to be 347γ. In a second experiment, carried out under the same conditions, the density excess of the combustion water was 354γ. The mean density excess of the combustion water was 350γ.

The presence of deuterium in the polyester after the reaction, which is indicated by the appreciable density excess of the combustion water, is an indisputable proof that an exchange reaction, involving the ester linkages occurs between polyhexamethylene sebacate and diethyl succinate-2,3-$\underline{d}_2$ since only in that case could the deuterated ester enter into the composition of the polyester, i.e. be found in the chemically bound state and therefore not be separable by physical methods. As control experiments have shown that a very small amount of diethyl succinate 2,3-$\underline{d}_2$ will nevertheless be retained by the polyester, as may be seen from the density excess of 30γ found in these experiments, it must be assumed that an equivalent density excess of 320γ for the polyester after reaction will characterize the extent of the exchange that occurred between the polyester and diethyl succinate-2,3-$\underline{d}_2$. If complete (100 %) exchange had occurred, the density excess of the combustion water of the polyester after reaction would have been 1000γ. In our case, therefore, about 30 % of the polyester entered into the exchange reaction with diethyl succinate-2,3-$\underline{d}_2$.

SUMMARY

1. An investigation has been made of the exchange reaction between polyhexamethylene sebacate and diethyl succinate-2,3-$\underline{d}_2$.

2. It has been proved that exchange reactions involving ester linkages occur during the course of the polyesterification process.

3. A convenient method has been developed for the preparation of diethyl succinate-2,3-$\underline{d}_2$.

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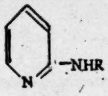
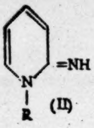
RELATIVE BASICITIES OF NITROGEN ATOMS IN COMPOUNDS OF THE 2-AMINOPYRIDINE AND 1-ALKYL-2(1H)-PYRIDONIMINE TYPES

Ya. L. Goldfarb, M. A. Pryanishnikova, and K. A. Zhukova

One of the distinguishing characteristics of compounds of the 2-aminopyridine (I) and 1-alkyl-2(1H)-pyridonimine (1-alkyl-1,2-dihydro-2-iminopyridine) (II) types, as systems containing the amidine grouping, is that in their stable salts they function as monoacid bases.



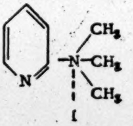
(I)



(II)

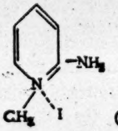
Thus, the molecule of the potentially diacid base (I or II) is able to hold firmly only one proton. This phenomenon, as such, has been satisfactorily explained with the aid of the concept of inductive inactivation [1], but the question of which of the two nitrogen atoms plays the part of the salt-forming center could not be regarded as solved until recently.

In 1947 one of the authors of this communication, together with Setkina and Danyushevsky, concluded on the basis of the results of absorption-spectra studies [2, 3], that in salts of compounds of Type I the proton is bound to the ring nitrogen (the example studied was a salt of 2'-aminonicotine). This conclusion was based on the following experimental results: a) the absorption maximum of 2-aminopyridine (I) is displaced toward the long waves in comparison with that of pyridine by about 400 A; and b) the absorption curves of the methiodide of 2-dimethylaminopyridine (III)



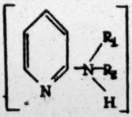
(III)

and pyridine are practically identical with respect to the positions of their absorption maxima, and similar coincidence of the curves is observed also for the pair — methiodide of aminopyridine (IV) and 2-aminopyridine (I):

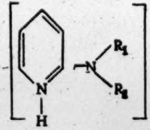


(IV)

It follows from these facts that salts belonging to the types (V) and (VI)



anion (V)



anion (VI)

(R_1 and R_2 may be H) should be quite distinct from one another in their absorption spectra, since the first (V) having a quadrivalent side-chain nitrogen is an analog of the methiodide (III), whereas the second (VI) is an analog of the methiodide IV.

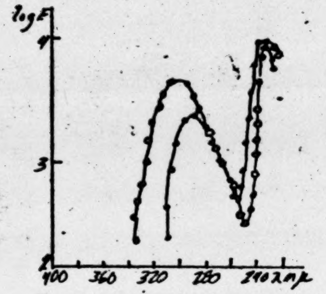


Fig. 1. ●—●—●— 2-aminopyridine in heptane; o—o—o—the same in 0.04 N hydrochloric acid.

The hydrochloride of 2'-aminonicotine, which is a substituted 2-aminopyridine, differs insignificantly spectrally from 2'-aminonicotine itself [3]. It was this fact that served as a basis for the above-mentioned conclusion concerning this salt.

The absorption spectra of unsubstituted 2-aminopyridine, as will be seen from our results (see Table 1) and results obtained from the literature,* have the same character in a number of nonaqueous solvents, and when these are replaced by dilute hydrochloric acid, only an insignificant bathochromic shift is to be observed (Fig. 1). Since in this case also there is no displacement toward the short waves when salt formation occurs, the inferences made for 2'-aminonicotine can be extended also to 2-aminopyridine: the salt-forming center is again the ring nitrogen. In these respects the properties of 2-aminopyridine are repeated by derivatives having substituents in the amino group, i.e., 2-methylaminopyridine and 2-benzylaminopyridine (Figs. 2 and 3).

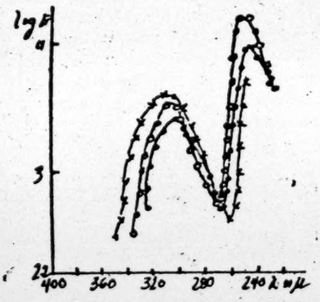


Fig. 2. ●—●—●— 2-methylaminopyridine in heptane; o—o—o— the same in dioxane; x—x—x— the same in 0.04 N hydrochloric acid.

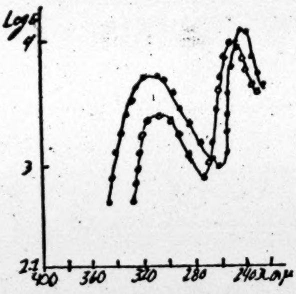


Fig. 3. ●—●—●—2-benzylaminopyridine in 0.04 N hydrochloric acid; o—o—o— the same in dioxane

It may be considered that the tendency for the proton to be bound by the ring nitrogen atom will be found in the majority of the bases of Type 1 (R=H, alkyl, or aralkyl), departures from this rule being, of course, possible when certain steric factors operate.

Compounds of Type II are stronger bases than those of Type I. This is shown, in particular, by the fact that the former, in contrast to the latter, form carbonates that are stable at ordinary temperature [4]. The very fact of the change in basicity observed for every pair of isomeric bases (I and II) may be regarded as evidence that a new salt-forming center has arisen. Such a view was in fact advanced by Goldfarb and Danyushevsky [4], who considered that the salt-forming center in bases of Type (II) was at the doubly-bound side-chain nitrogen. The experimental results of the present investigation confirm this point of view.

As will be seen from the results given in the table, these systems differ spectrally from systems of Type (I) in that their absorption maxima preserve their positions in each of the two groups of solvents (heptane, dioxane and ether; ethanol, water, hydrochloric acid), but are appreciably displaced when a solvent of the first group is replaced by one of the second. Setkina, Danyushevsky, and Goldfarb, studying for the first time the absorption

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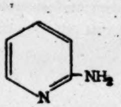
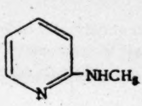
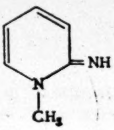
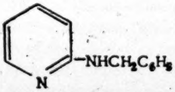
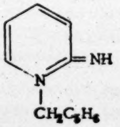
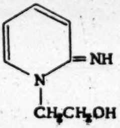
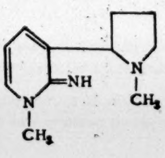
* The results of other authors are distinguished by the insertion of a source reference number in the seventh column of the table.

TABLE

Substance	Formula	max$_1$ λ (mμ)	Log E	max$_2$ λ (mμ)	Log E	Reference
2-Aminopyridine:						
in heptane		290	3.4	234	4	
in ether		298	~3.6	–	–	[5]
in dioxane		296	3.5	238	4.1	
in dioxane + water *		295	3.7	238	4.1	
in ethanol		293	3.6	–	–	[2]
in 0.04 N hydrochloric acid		301	3.7	233	3.9	**
2-Methylaminopyridine						
in heptane		298	3.4	244	4	
in ether		300	3.7	–	–	[5]
in dioxane		303	3.5	245	4.2	
in dioxane + water		305	3.3	245	4.2	
in ethanol		306	3.6	–	–	
in 0.04 N hydrochloric acid		306	3.6	–	–	
in water		302	3.4	238	4.0	
1-Methyl-2(1H)-pyridonimine						
in heptane		346	3.2	257	3.8	
in ether		350	3.5	–	–	[5]
in dioxane		345	3.3	255	4.1	***
in dioxane + water		346; 302	3.3; 3.4	250	3.8	***
in 0.04 N hydrochloric acid		299	3.6	–	–	[3]
in ethanol		300	3.9	–	–	
2-Benzylaminopyridine						
in dioxane		306	3.4	247	4	
in dioxane + water		307	3.5	246	4	
in 0.04 N hydrochloric acid		309	3.7	238	4.1	
1-Benzyl-2(1H)-pyridonimine						
in heptane		350	3.4	255	3.7	
in dioxane		353	3.5	257	3.8	
in dioxane + water		305	3.6	237	3.8	
in 0.04 N hydrochloric acid		300	3.7	–	–	
1-(2-Hydroxyethyl)-2(1H)-pyridonimine						
in dioxane		350	3.5	258	4	
in dioxane + water		305	3.6	235	3.7	
in ethanol		305	3.6	236	3.7	
in 0.04 N hydrochloric acid		302	3.7	–	–	
in water		303	3.6	238	3.6	
1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)pyridonimine						
in heptane		350	3.5	256	4	
in dioxane		350	3.6	258	4	
in dioxane + water		305	3.7	240	3.7	
in 0.04 N hydrochloric acid		310	3.7	235	3.8	
in water		305	3.7	234	3.7	

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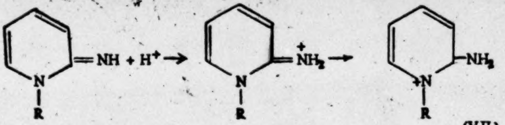
* Dioxane 70%, water 30%.

** See also [9].

*** See also [5].

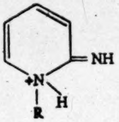
spectra of some bases of the 1-alkyl-2(1H)-pyridonimine type, observed a similar type of displacement when comparing the absorption curves for 1-methyl-2(1H)-pyridonimine in heptane and in alcohol [2], and later Anderson and Seeger observed a similar phenomenon when comparing the absorption spectra of this base in anhydrous and in aqueous dioxane [5].

In connection with the question under examination, it must be pointed out here that the absorption curves of pyridonimine systems in acid media are practically identical, with respect to the positions of the maxima, to the absorption curves of aminopyridine systems (Fig. 4, 5, and 6). This may be interpreted as due to the reaction of the former with acid to give the structure of the second (aminopyridine) type:



(VII)

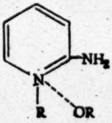
It will be seen that it is suggested in this scheme that the proton unites with the side-chain nitrogen atom, yielding, owing to simultaneous displacement of the double bond, a compound having the benzene bond system. If the proton had added at the ring nitrogen, an ion would have been formed of structure



having the same system of bonds as that of the original compound (Type II) and spectrally not distinguishable from it. Actually, compounds of structure II in heptane or dioxane give a band having a maximum at 3450-3500 A, whereas in acid the maximum is at about 3000 A.

From these results we may conclude that the side-chain nitrogen atom in molecules of bases of Type (II) has a greater affinity for a proton than the ring atom, and, since the affinity for a proton is the criterion for the strength of the base, we may speak of the relative or comparative basicity of these two atoms. It is relevant here to note the parallelism in properties between 1-alkyl-2(1H)-pyridonimines and simple amidines: in the latter also, according to Shigorin and Syrkin's results [6], the more basic nitrogen atom is the double-bound imine atom. The higher basicity of the side-chain nitrogen of compounds of Type (II) is evidently related to some extent to the tendency of the ion formed by addition of a proton at this point to pass into the energetically favored benzenoid system (see equation above).

In view of the fact that the absorption curves for 1-benzyl-2(1H)-pyridonimine and the isomeric 2-benzylaminopyridine, dissolved in each case in ethanol, are found to be coincident [3] and that the same applies to another pair of isomeric bases, 1-methyl-2(1H)-pyridonimine and 1-methylaminopyridine (see table and [2]), we may conclude that the same transformation occurs also when bases of Type II react with ethanol. The structure of the system formed (VIII)



(VIII)

should not differ spectrally from that of bases of Type (I) or of the salts of the structure (VII); this is found to be so when the relevant curves are compared (see the table and the curves in Fig. 7).

The coincidence of the absorption curves of aminopyridine and pyridonimine systems in alcohol and, as we shall see, in water may therefore be explained by the interaction of a base of the second type with the medium. In this connection, it should be noted that the explanation of the spectral identity of compounds of Types (I) and (II) given in the paper by Goldfarb, Danyushevsky, and Setkina [2,3], was incorrect, being based on a concept concerning the superposition of structures that is known to be erroneous; as we have seen, the absorption spectra of bases of the second type in media that do not react with them (dioxane, heptane, etc.), differ greatly from those of the 2-aminopyridine series.

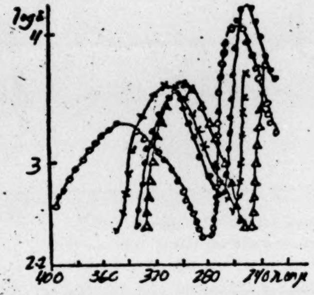


Fig. 4. ●—●—●— 2-methylaminopyridine in dioxane; x—x—x— the same in 0.04 N HCl; o—o—o— 1-methyl-2(1H)-pyridonimine in dioxane; Δ—Δ—Δ— the same in 0.04 N HCl.

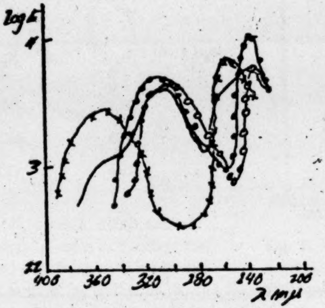


Fig. 5. x—x—x— 1-benzyl-2(1H)-pyridonimine in dioxane; o—o—o— the same in 0.04 N HCl; ——— the same in dioxane + water; ●—●—●— 2-benzylaminopyridine in 0.04 N HCl.

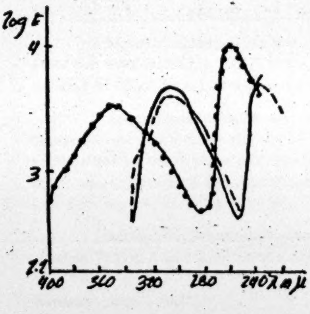


Fig. 6. ●—●—●— 1-(2-hydroxyethyl)-2(1H)-pyridonimine in dioxane the same in dioxane + water; ——— the same in 0.04 N HCl.

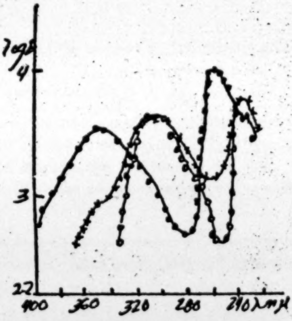
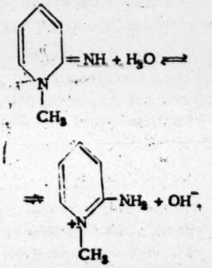


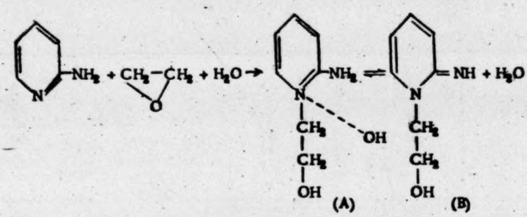
Fig. 7. ●—●—●— 1-(2-hydroxyethyl)-2(1H)-pyridonimine in dioxane; x—x—x— the same in ethanol; o—o—o— the same in water.

From the results given in the table and the curves in Figs. 5, 6, 7, and 8, it will be seen that substituted 2(1H)-pyridonimines (II) give absorption bands that are characteristic for 2-aminopyridine systems also in the cases in which water or aqueous dioxane is used as solvent. 1-Methyl-2(1H)-pyridonimine in aqueous dioxane, as was shown by Anderson and Seeger [5] and has been confirmed by us, gives not only the band corresponding to the 2-aminopyridine type of system, but also its own characteristic band with a maximum at 3450 A. In this case, therefore, we have an equilibrium system [5]:



The first, long-wave maximum, corresponding to systems of Type (II), is not found in all cases: this may be because the equilibrium is strongly displaced toward the aminopyridine structure.

When 2-aminopyridine reacts with ethylene oxide in alcohol [7] or in aqueous dioxane [8], 1-(2-hydroxyethyl)-2(1H)-pyridonimine is formed. In absence of water or alcohol, this reaction does not go [8]. Taking this fact into account and assuming also that 2-aminopyridine reacts only in the aminopyridine form [2], Goldfarb and Pryanishnikova have suggested [8], the following scheme for the mechanism of the formation of this base:



An attempt to isolate the base (A), as such, could not, of course succeed; it was therefore necessary, in order to confirm that it was possible for the process to proceed according to this scheme, to make sure that the base(B) was able to give, by hydration, a quaternary base of structure (A). The results given in the table and by the curve in Fig. 7, provide evidence in support of the view that in solvents of the water type, 1-(2-hydroxyethyl)-2(1H)-pyridonimine, which gives a band that is characteristic for aminopyridine systems, reacts with the solvent forming a quaternary base of the type (A).

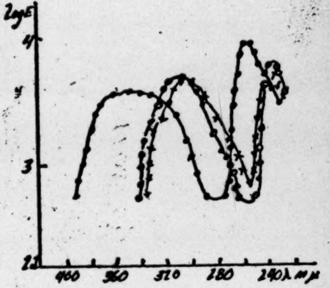


Fig. 8. ●—●—●— 1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridonimine in dioxane; x—x—x— the same in dioxane + water. o—o—o— the same in 0.04 N HCl.

EXPERIMENTAL

1. Chemical Part of the Work

2-Methylaminopyridine was prepared by the method of Chichibabin and Knunyants [10]; it had a b.p., after two distillations, of 92°/11 mm. 1-Methyl-2(1H)-pyridonimine, b.p. 90°/6 mm, was prepared by the method of Chichibabin, Konovalova and Konovalova [11].

2-Benzylaminopyridine was prepared by the method of Chichibabin and Knunyants [12]. The product was recrystallized twice from alcohol and then melted at 94°. 1-Benzyl-2(1H)-pyridonimine, b.p. 169°/6 mm, was synthesized by the method of Chichibabin, Konovalova, and Konovalova [11]. 1-(2-Hydroxyethyl)-2(1H)-pyridonimine was obtained by Knunyants' method [7]. The substance was crystallized three times from absolute alcohol, and then melted at 127.5–128.5°.

1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridonimine was prepared by Goldfarb and Kondakova's method [13] and was purified via the carbonate. After being liberated from this salt, it was again vacuum-distilled, b.p. 144-147°/3 mm. 2-Aminopyridine was purified by vacuum distillation and recrystallization from heptane; m.p. 57-58°.

The solutions required for the spectrum determinations were prepared under conditions that excluded the entry of carbon dioxide and moisture from the air. Weighed amounts of the pyridonimines were taken in microcapillaries, which were then broken under the solvent, the air in the flask having been previously displaced by nitrogen.

2. Optical Part of the Work

The spectra were photographed on a medium-sized Hilger spectrograph. The dispersion of the spectrograph was 44 mμ/mm at 360 mμ, and 12 mμ/mm at 250 mμ. The light source was a tungsten arc. The dimensions of the slide of the spectrograph were 13 x 18 cm, and isoortho plates, sensitivity 400, were used. The developer was of the metal–hydroquinone type, and the fixing bath was acid. The spectra were measured by the "equal blackening" method. A quartz Hüfner rhomb served for dividing the light beam. Variation in the intensity of the comparison beam was effected with the aid of a rotating sector. The places of equal blackening were found visually. The wavelength scale was provided by the spectrum of a copper arc. Every spectrum was measured several times, and the result was considered to be satisfactory when the points found from the last photograph of the spectrum fitted closely to the curve obtained from previous photographs. The concentration of the solution of a compound investigated was altered by factors of 10 and 100.

We feel that it is our duty to express our deep gratitude to Prof. E. V. Shpolsky for making it possible for us to carry out the optical part of the work in the optical laboratory of which he is director; also for his interest in our work.

SUMMARY

1. It has been shown, by comparison of the absorption spectra of compounds of the 2-aminopyridine series and the 2(1H)-pyridonimine series in various media, that the salt-forming center in bases of the first type is to be found at the ring nitrogen atom, whereas in bases of the second type it is to be found at the side-chain nitrogen.

2. When substituted 2(1H)-pyridonimines are dissolved in dilute acid or in alcohol (or water [5]), they assume structures of the 2-aminopyridinium salt type.

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[10] A. E. Chichibabin and I. L. Knunyants, Ber. 61, 2215 (1928).

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[12] A. E. Chichibabin and I. L. Knunyants, Ber. 64, 2839 (1931).

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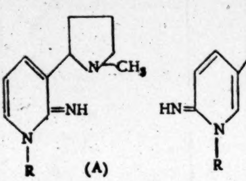
RELATION BETWEEN THE STRUCTURES OF CERTAIN ORGANIC BASES AND THEIR ABILITY TO FORM ADDITION COMPOUNDS WITH CARBONIC ACID

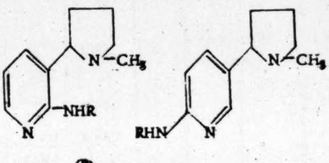
COMMUNICATION 2. PYRIDINE DERIVATIVES

Ya. L. Goldfarb and Ya. L. Danyushevsky

The results of a study of the action of carbonic acid on certain nicotine derivatives, which were presented in the first communication [1], led us to the following conclusions: 1) bases having the 2(1H)-pyridonimine (1,2-dihydro-2-iminopyridine) system of bonds (A) are precipitated from their solutions in ether or acetone by carbonic acid, yielding salts relatively stable at room temperature; 2) bases having the isomeric structure (B) are not precipitated from their solutions in these solvents by carbonic acid at room temperature; 3) in the salts mentioned the salt-forming center is at the doubly bound side-chain nitrogen; and 4) the compounds formed by addition of carbonic acid to nicotonimines are carbonates, not carbamates.



(A)



(B)

It was considered desirable to determine the extent to which these conclusions applied to analogous compounds of the pyridine series, in which the basic properties are associated with the presence in the molecule of only the two nitrogens of the amidine grouping and are not subject to the influence of the third nitrogen atom that is present in bases of types A and B. The results of the experiments that we accordingly carried out are given in the table; for convenience, they are arranged so that comparisons may readily be made between the members of each pair of isomeric bases with respect to their behavior toward carbonic acid.

Examination of these results shows, first of all, that, as in the case of the corresponding nicotine derivatives, 1-alkyl- and 1-aralky-2(1H)-pyridonimines form carbonates that are stable at room temperature. Thus, from a very dilute ethereal solution of 1-methyl-2(1H)-pyridonimine containing the necessary amount of water, precipitation of the salt begins as soon as passage of CO_2 begins; precipitation is about 90% complete* at room temperature, and the yield may be further increased to 94-95% by lowering the temperature to −10-15°. 2-Methylaminopyridine (II), which is isomeric to (IIa), is not precipitated at room temperature, even from a relatively concentrated solution; only when the temperature is lowered to −30-35° is a turbidity to be observed in the solution, and a thin layer of oil is formed, which immediately gives up CO_2 to the air. The nature of the product formed in this case, and also that of the crystalline compound formed from 2-aminopyridine (I) at low temperature, could not be established owing to the high instability of these substances. In view of the other results given in the table and in the first communication [1], we may suggest only that these products are not salts of the tautomeric, pyridonimine forms of 2-aminopyridine or 2-methylaminopyridine, since salts of this type are stable at room temperature. The behavior observed for the isomeric pairs of bases (III) and (IIIa), and (IV) and (IVa) is similar to that of the pair (II) and (IIa).

2-Benzylaminopyridine (III) is not precipitated by carbonic acid at ordinary temperatures, even from a 3% solution, and when the temperature is lowered the precipitate formed is not a salt, but unchanged base. The

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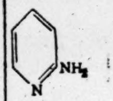
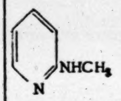
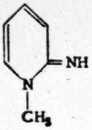
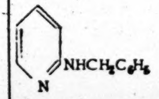
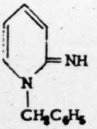
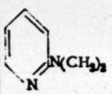
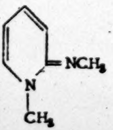
* The yields given in the text relate to the amount of salt obtained by saturation of a solution of the concentration indicated in the table with carbon dioxide.

TABLE *

Compound No.	Base	Solvent	Amt. substance per 100 ml of solvent (g)	Limit of lowering temp. (°C)	Precipitation		Stability of addn. prod. at room temp.	Reaction with Ba++	Found (%)		Calculated (%)	
					S	S+H_2O			C	H	C	H
1	2	3	4	5	6	7	8	9	10	11	12	13
(I)		E	1.5; 2.0	−40 −50	cr. ppt.	cr. ppt.	unstab.	+				
(II)		E	20.0	−30 −35	—	oil	unstab.	+				
(IIa)		E	1.0; 2.0	room	—	cr. ppt.	stab.	+	44.65 44.72	6.31 6.51	44.68 $C_6H_8N_2 \cdot H_2CO_3 \cdot H_2O$	6.38
		A	1.0; 2.0	room		cr ppt	stab.	+				
		EA	2.0	room		ditto	stab.	+				
		D	2.0	room		ditto	stab.	+				
		P	2.5	room		ditto	stab.	+				
(III)		E	1.0; 3.0	−15 −25	—	orig. base						
		A	10.0	−5	—	—						
(IIIa)		E	1.5; 4.0	room		cr. ppt.	stab.	+	63.07	5.73	63.41	5.69
		A	1.5	room		cr. ppt.	stab.	+	63.44	5.78	$C_{12}H_{12}N_2 \cdot H_2CO_3$	
(IV)		E	3.0	−50		—						
		E and A 1:1	14.0	−50	—	—						
(IVa)		E	1.6	room	—	cr. ppt.	stab.	+	47.23	6.89	47.52	6.93
		A	1.3	room	—	ditto	stab.	+	47.56	6.71	$C_7H_{10}N_2 \cdot H_2CO_3 \cdot H_2O$	

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* See page 140 for footnote and key to abbreviations.

TABLE – (continued)

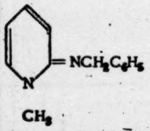
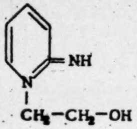
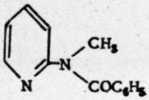
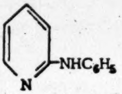
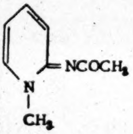
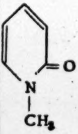
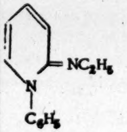
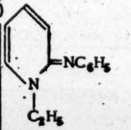
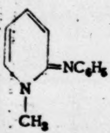
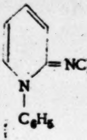
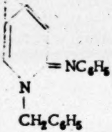
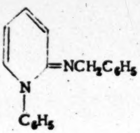
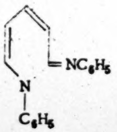
1	2	3	4	5	6	7	8	9	10	11	12	13
(V)		E	1.7; 2.0	room	—	cr. ppt.	stab.	+	60.30 60.52	6.38 6.50	60.43 $C_{13}H_{14}N_2 \cdot H_2CO_3H_2O$	6.47
		A	1.5; 5.0	0−10	—	ditto	stab.	+				
(VI)		A	1.1	room	—	ditto	stab.	+	48.23 48.31	6.08 6.14	48.00 $C_7H_{10}N_2O \cdot H_2CO_3$	6.00
(VII)		E	14.6	−40 −50	—	orig. base						
		A and E 2:1	7.0	−50		—						
(VIII)		A	7.0	−35	—	orig. base						
(IX)		E	1.0	+3 - +5	—	oil	unstab.	+				
		A	6.0	−30 - −45	—	oil	unstab.	+				
(X)		A	10.0	−50	—	—						
		E and A 1:1	5.0	−50		—						
(XI)		E		−10 −12		oil	unstab.	+				
(XII)		E	10.0; 20.0	−35	—	mixture of oil and cr. ppt.	unstab.	+				

TABLE -- (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
(XIII)		E	1.5: 2.0	−25 −40		cr. ppt.	stab.	+	62.16	6.14	63.41	5.69
		A	1.0: 8.0	−25 −40		ditto	stab.	+	61.89	6.07	$C_{12}H_{12}N_2 \cdot H_2CO_3$	
(XIV)		E	1.0	room	−	oil		+				
(XV)		E	2.5	−0 −5	−	orig. base						
		E and A 3:1	2.5	−50		orig. base						
(XVa)		E	1.0	room		oil		+				
(XVI)		E	1.0	−50		orig. base						
		B and E 2:3	4.0	−40		orig. base						
		A	3.0	−40- −50		orig. base						

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* For information concerning apparatus and procedure see the first communication [1]. The concentrations of the solutions were chosen so that the aminopyridine base was treated under the more favorable conditions for precipitation; in some cases, however, it was not possible to obtain a solution of the desired concentration, owing to the limited solubility of the base. The amount of water introduced was 1.2 moles per mole of base. At low temperature a part of it froze out, but this did not affect the course of the precipitation. The time during which carbon dioxide was passed varied from 30 minutes to several hours, depending on the observed rate of precipitation.

Abbreviations: S, dry solvent; E, ether; A, acetone; D, dioxane; EA, ethyl acetate; P, pyridine; B, benzene; −, does not precipitate; cr. ppt., crystalline precipitate (underlined, rapid precipitation; not underlined, slow precipitation); stab., stable; unstab., unstable, rapidly decomposing in the air with evolution of CO_2; +, positive; orig. base, original base.

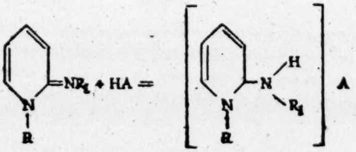
isomeric 1-benzyl-2(1H)-pyridonimine, however, begins to be precipitated from its 2% solution in ether already at room temperature: the yield of salt may then reach 30%, but by lowering of the temperature to −10 - −15° the yield may be raised to 95%. 2-Dimethylaminopyridine (IV) is not precipitated from its dilute ether solution, or relatively concentrated ether—acetone solution, even when the temperature is lowered to −50°. The isomeric N^2,1-dimethyl-2(1H)-pyridonimine (IVa) forms a stable salt in 80% yield from ether solution at room temperature; the yield from acetone solution is about 57%.

In this last case, since the possibility of the formation of carbamate is excluded and the addition product is formed with participation of water, it may be regarded as established that it is a carbonate. A similar conclusion can be made on the basis of analogy for other stable carbonic acid addition compounds that are characterized in the table. In this connection it should be noted that these addition products have the characteristic property of being soluble in water.

It will be seen from these considerations that we have treated the nonappearance of a precipitate when the ether solution of a base was saturated with carbonic acid as an indication that the salt was unstable under the given conditions. It may be supposed that in our experiments the main factor determining the behavior observed was the degree of instability of the salt, and not its solubility. Generally speaking, the carbonates of 1-alkyl-2(1H)-pyridonimines are practically insoluble even in moist ether; thus, when the carbonate of 1-benzyl-2(1H)-pyridonimine (IIIa) is heated with ether, only traces of base, formed by decomposition of the salt, pass into solution. The solubilities of the carbonates of the isomeric 2-alkylaminopyridines could not be directly determined, since such salts were not accessible at room temperature. Since, however, compounds of the 2-aminopyridine structure, such as 2-benzylaminopyridine (III), are less soluble in ether than those having the isomeric pyridonimine structure (IIIa), it may be supposed that the ether-solubility of salts of the base (III) will in any case be not greater than that of salts of the base (IIIa). We have seen that at room temperature a salt is precipitated from a solution of 1-benzyl-2(1H)-pyridonimine (IIIa) when it is saturated with carbon dioxide, whereas a solution of (III) remains unchanged under these conditions; the whole course of these considerations, therefore, leads us to the conclusion that the carbonate of 2-benzylaminopyridine is either not formed, or is unstable, at room temperature.

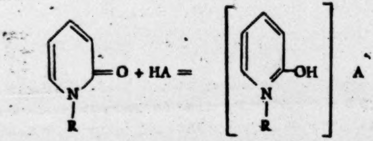
In the light of the above considerations, the relation of the compounds (V, VI, and VII) to carbonic acid becomes clear. The first two compounds, which belong to the 1-alkyl-2(1H)-pyridonimine series, are precipitated from ether or acetone solution with formation of stable carbonates, but the compound (VII), which is an acyl derivative of 2-methylaminopyridine, and the compound (VIII), do not form salts even at very low temperatures.

The presence in the molecule of 2-aminopyridine, or one of its derivatives, of an amidine grouping, is revealed by a number of properties, which permit a clear demarcation to be made between the province of bases of this type and that of bases of the 3-aminopyridine series. It is well known, for example, that stable salts of 2-aminopyridine bases contain one, and not two equivalents of acid. The cause of this phenomenon, according to Mann [2], is to be found in the inductive effect due to the positive charge on the nitrogen attached to the proton of the acid; this explanation, however, leaves open the question of which of the two nitrogen atoms of the 2-aminopyridine system is the salt-forming center. On the basis of a study of the absorption spectra of a number of pyridine and nicotine derivatives, we, with Setkina, concluded that the proton unites to the ring nitrogen atom (the compound for which this was demonstrated was 2'-aminonicotine) [3]. From these and other results [4] it may be shown that the molecule of 1-alkyl-2(1H)-pyridonimine unites with a proton through the side-chain nitrogen atom:



In view of these facts, it was considered to be of interest to examine the behavior toward carbonic acid of a number of substituted 2(1H)-pyridonimines whose main function had been weakened by the introduction of an electronegative radical into the amidine grouping. One of the members of this group, N^2-acetyl-1-methyl-2(1H)-pyridonimine (IX), is precipitated at low temperature from ether or acetone in the form of an oil, which gives up carbon dioxide at room temperature. Thus, weakening of the basic properties due to introduction of an acetyl group into the 1-methyl-2(1H)-pyridonimine (IIa) molecule is still insufficient to deprive it of the ability to be precipitated by carbonic acid (from an approximately 1% solution in ether) at a temperature close to 0°.

As we have already seen, 1-alkyl-2(1H)-pyridonimines form salts by accepting a proton at the side-chain (not ring) nitrogen atom. One of the causes of this phenomenon is evidently that only this type of addition ensures the formation of a compound having the energetically favorable benzenoid bond system (see the above equation). It is quite possible that this factor plays an important part also in the reaction of acids with 1-alkyl-2(1H)-pyridone, i.e., in this case also, the process is favored by the formation of a stable benzenoid system. It is quite clear that a system of this type could be obtained simply by the addition of a hydrogen ion at the oxygen atom of the 1-alky-2(1H)-pyridone molecule:



This view of the structure of salts of 1-substituted 2(1H)-pyridone [5] is confirmed by the results of Specker and Gawrosch [6] on the absorption spectra of N- and O-substituted 2(1H)-pyridone. It is of interest in this connection to note that the hydrochloride of 1-methyl-2(1H)-pyridone, like 2(1H)-pyridone [8], shows a coloration with ferric chloride [7, 9].

On the basis of these considerations it was considered desirable to include 1-methyl-2(1H)-pyridone among the compounds to be studied. Actually, the formation of a stable carbonate in this case would serve as a further confirmation of the suggested structure of the salt, although, if the carbonate were found to be unstable, this would not, of course, mean that the formula cited must be regarded as unsatisfactory.

1-Methyl-2(1H)-pyridone has been described as a strong base that absorbs carbon dioxide from the air [7, 9]. Our observations (see the table) are not in accord with such a description of the compound: when its solution in ether or ether—acetone mixture is saturated with carbon dioxide, no turbidity or precipitate is to be observed even when the temperature is lowered to −50°. It is still not clear to us what conditions must be observed for the formation of a salt, as described by Fischer and Chur [9], when carbon dioxide is passed through an ether solution of 1-methyl-2(1H)-pyridone.

Since the salt-forming center of the 2(1H)-pyridonimine molecule is the side-chain nitrogen atom, it may be expected that the effect of an aryl radical (lowering of the stability of the carbonate) will be greater when it is attached to this nitrogen, and not to the ring nitrogen atom. For the compounds that were accordingly examined, 1-ethyl-N^2-phenyl-2(1H)-pyridonimine (XII) and N^2-ethyl-1-phenyl-2(1H)-pyridonimine (XI), we could not, however, find any notable difference in their behavior toward carbonic acid. In this connection it should be noted that the observation of the tendency of phenyl-substituted 2(1H)-pyridonimines to be precipitated is rendered difficult, in general, by the fact that their addition products with carbonic acid are precipitated very slowly and in the form of oils. An exception in this respect is 1-methyl-N^2-phenyl-2(1H)-pyridonimine (XIII), which forms a crystalline carbonate that only slowly loses carbon dioxide; the analytical results for this compound are not fully in accord with those calculated from the formula, but the discrepancy is small.

A clearer picture of the effect of the aryl radical is to be observed in the case of two other substituted 2(1H)-pyridonimines, 1-benzyl-N^2-phenyl-2(1H)-pyridonimine (XV) and N^2-benzyl-1-phenyl-2(1H)-pyridonimine (XVa). The second of these compounds is precipitated from ether solution by carbonic acid in the form of an oily addition product already at room temperature, whereas the first is precipitated unchanged at low temperature.

The effect of a second aryl radical, not directly bound to the side-chain nitrogen of a substituted 2(1H)-pyridonimine, on the stability of the salt may be examined by a comparison of the results of experiments on the action of carbonic acid on 1-methyl-N^2-phenyl-2(1H)pyridonimine (XIII) and N^2-1-diphenyl-2(1H)-pyridonimine (XVI).

In conclusion, the authors consider it necessary to emphasize that, since the stability of the carbonic acid addition products could be determined only approximately and the observation of the course of the precipitation was difficult in a number of cases, the conclusions reached on the basis of the results presented can serve only as a general qualitative characterization of the behavor of substituted 2(1H)-pyridonimines and their isomers of the 2-aminopyridine series toward carbonic acid.

SUMMARY

1. It has been shown that certain substituted 2(1H)-pyridonimines are precipitated at room temperature by carbonic acid from their solutions in ether or acetone.

2. It has been shown that the addition products formed in this way between carbonic acid and the bases are stable at room temperature and are the carbonates of the bases.

3. Bases of the 2-aminopyridine series are not precipitated at room temperature by carbonic acid from their solutions in ether or acetone.

4. The introduction of a phenyl or acetyl radical into the amidine grouping of 1-methyl (or benzyl)-2(1H)-pyridonimine does not lead to loss of the ability of the compound to be precipitated by carbonic acid.

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THEORY OF TAUTOMERIC EQUILIBRIUM

COMMUNICATION 3. THE QUESTION OF PSEUDOMERISM. STRUCTURE AND PROPERTIES OF DIALKYL THIOPHOSPHITES

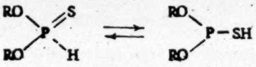
M. I. Kabachnik and T. A. Mastryukova

I

One of us has recently shown that prototropic tautomeric equilibrium belongs to the protolytic acid–base type. In equilibrium there are two acids, which both give the same anion, and a solvent or other base present in the solution is the carrier of the proton. The tautomeric equilibrium constant is the ratio of the ionization constants of the tautomeric forms in the given solvent S [1, 2].

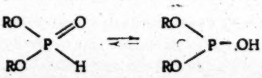
In the problem of tautomerism the question of the effect of the position and rate of establishment of the equilibrium is of great significance for the course of chemical reactions. In this respect particular interest is presented by equilibrium mixtures for which the position of equilibrium is strongly displaced in one direction; these occur when the forms differ greatly in their ionization constants: the position of equilibrium is displaced in the direction of the less acidic form, and the greater the difference in the ionization constants, the greater the displacement will be.

We have investigated the chemical properties of such a tautomeric pair for the case of dialkyl thiophosphite [dialkyl phosphonothionate (I) and O,O-dialkyl hydrogen phosphorothioite (II):



(I) (II)

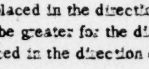
which we recently synthesized from tetraphosphorus heptasulfide and alcohols [3]. Dialkyl thiophosphites are sulfur analogs of dialkyl "phosphites" (dialkyl phosphonate III and dialkyl hydrogen phosphite IV):



(III) (IV)

The question of the tautomerism of these and their chemical properties have been studied in detail by many chemists, particularly by A. E. Arbuzov and his students [4]. The general opinion is that the tautomeric equilibrium of the dialkyl phosphites is considerably displaced in the direction of the form (III). As the difference in acidic properties between the tautomeric forms must be greater for the dialkyl thiophosphites than for their oxygen analogs, the equilibrium must be still more displaced in the direction of the phosphonic form (I).

We wished to find chemical reactions of dialkyl thiophosphites that would give an unequivocal indication of the part played in the reaction by the form (II). We presumed that, as this form was consumed in the reaction, the equilibrium would be constantly reestablished, until the whole of the dialkyl phosphite had undergone the reaction characteristic for the form (II). In particular, the form (II) should be responsible for various addition reactions: the addition of sulfur, cuprous halides, alkyl halides, etc., which is so characteristic for tervalent phosphorus compounds [5] and is not in any way peculiar to quinquevalent phosphorus. Dialkyl thiophosphites, however, did not undergo any of these addition reactions. Of those properties that might be ascribed to the presence of the form (II) we found only one: the ability of diethyl thiophosphite to form metal derivatives (sodium, silver), the structure of which is generally accepted to be that of formula (V).



$(C_2H_5O)_2P-S-Na$

(V)

It was found, however, that the sodium salts did not correspond in their behavior toward water to salts of a relatively strong acid, such as the form (II) would be expected to be: they were immediately hydrolyzed by water. The results obtained led us to the conclusion that in this greatly displaced equilibrium, such as the equilibrium (I) $\rightleftarrows$ (II) must be, the chemical properties of the form (II) are almost completely suppressed, evidently owing to the low value of its effective concentration. This conclusion, however, was in conflict with the generally accepted concept of pseudomerism.

II

The concept of pseudomerism was introduced into science at the end of last century, following the work of Bayer on isatin [6]. It related to the phenomena exhibited by a substance, such as isatin, known in only one form, but forming two series of derivatives, corresponding in structure to two possible tautomeric forms.

Later, when it had been confirmed that tautomerism is nothing more than equilibrium isomerization — a phenomenon discovered by Butlerov [7] long before the appearance of the tautomerism concept — the term "pseudomerism" began to be understood as relating to very much displaced, but rapidly established, tautomeric equilibria, in which the concentration of one of the forms is so low that it cannot be measured by any of the usual chemical or physical methods ("immeasurably low", "vanishingly low", etc., concentrations), but, owing to the high reactivity of this form and the rapidity with which equilibrium is established, this form enters into particular chemical reactions and so forms its own series of derivatives.

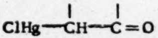
This concept of pseudomerism appears to have been introduced by Knorr [8]. It was particularly systematically developed by Ingold and Thorpe [9], and it has received wide acceptance. It has even been suggested that the position of the equilibrium A $\rightleftarrows$ B may be "anywhere" [10] and it will still be possible to treat the conversion of A into B' in terms of the pseudomeric change

$$A \rightleftarrows B \longrightarrow B',$$

it is only necessary to assume sufficiently high rates of conversion.

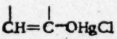
From a certain time all cases in which a substance is in fact known only in one form but forms two series of derivatives began to be explained by the pseudomerism concept. This extreme point of view is taken in, for example, Baker's book "Tautomerism" [11].

How erroneous this generalization is has been shown by recent investigations by Nesmeyanov, Lutsenko, Sazonova, and others. They have shown that two series of derivatives may be formed when tautomeric relationships are completely absent. For example, α-mercurated aldehydes and ketones having the keto structure (VI)



$$ClHg-\overset{|}{C}H-\overset{|}{C}=O$$

(VI)



$$\overset{|}{C}H=\overset{|}{C}-OHgCl$$

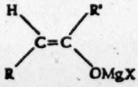
(VII)

which are not capable of reversible conversion into the mercury derivatives of the corresponding enol forms (VII), are able, depending on the nature of the reagent, to give both C- and O-derivatives, for example (VIII) and (IX) [12]:

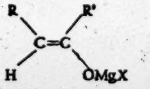
$$(C_6H_5)_3C-CH_2-CHO \qquad CH_2=CH-O-C(C_6H_4NO_2)_3$$

(VIII) (IX)

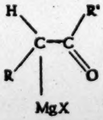
Again, stereoisomeric (cis-trans) magnesium (lithium, sodium) enolates of certain ketones (X and XI) are incapable of reversible conversion into the corresponding organometallic keto forms (XII) (this follows from the fact that the stereoisomers do not undergo interconversion under the conditions studied).



(X)

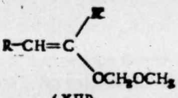


(XI)

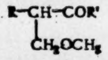


(XII)

They are able, however, to form both O- and C-derivatives, for example in methoxymethylation (XIII and XIV) [13]:



(XIII)



$$R-\underset{\displaystyle CH_2OCH_3}{\underset{|}{CH}}-COR'$$

(XIV)

the first of which preserves the stereoisomeric relationships.

If in the investigations cited there had been no convincing proof of the absence of tautomeric relationships, the results obtained could have been readily explained in terms of the concept of the pseudomerism of metal salts, in the same way as Hückel, for example, has explained the C-alkylation of salts of keto-enol compounds [14]. However, there are no tautomeric relationships here. According to Nesmeyanov, the explanation of the formation of two series of derivatives in absence of tautomerism (in this and other cases) must be sought in the tendency in molecules containing conjugated bonds to undergo "transfer of reaction center" at the moment of reaction under the influence of the attacking reagent and under definite conditions in the reaction medium [15, 16, and 17].

On the basis of these investigations by Nesmeyanov and coworkers, it may be regarded as proved that there are at least two ways in which two series of derivatives (for example, keto and enol) may be formed: first by reversible isomerization with subsequent formation of derivatives from the respective tautomeric forms (keto from the keto forms, and enol from the enol forms); and second by direct formation of keto derivatives from enol forms (or from enolate ions) or enol derivatives from keto forms, which results from reaction proceeding in one elementary act with transfer of reaction center.

Generally speaking, both methods of derivative formation are possible in displaced tautomeric equilibria. It may be shown, however, that in strongly displaced (pseudomeric) tautomeric equilibria, the first method — via preliminary tautomerization — becomes very improbable.

Let us examine a pseudomeric equilibrium between two forms A and B, strongly displaced in the direction of A. Let B react to give B':

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_3} B'.$$

There are numerous experimental results showing that tautomeric transformations proceed, formally, as reactions of the first order. As regards the reaction $B \longrightarrow B'$, this may be of a different order. Let us consider a system of two successive reactions, of which the first is of the first order and is reversible, and the second is either of the first or the second order. Let c_0 be the initial concentration (total), a_0 and b_0 the initial concentrations of the forms A and B [$a_0 + b_0 = c_0$], c, a, b, and b' the corresponding current concentrations [$a + b = c$], k_1 and k_2 the rate constants of the forward and back reactions of the tautomeric change, k_3 the rate constant of the unimolecular reaction $B \longrightarrow B'$, k_3' the rate constant of the bimolecular reaction $B + R \longrightarrow B'$; and r_0 and r the initial and current concentrations of the reagent R.

For the equilibrium constant of $A \rightleftarrows B$, we have:

$$K_T = \frac{b_0}{a_0} = \frac{k_1}{k_2}.$$

We have also the conditions that $k_2 \gg k_1$ and $a_0 \gg b_0$.

A) If the transformation $B \longrightarrow B'$ proceeds much more rapidly than $B \longrightarrow A$, i.e. $k_3 \gg k_2$ or $k_3' r \gg k_2$, the rate of the whole process is limited by the transformation $A \longrightarrow B$. Hence the rate of formation of B' at any given moment will be equal to (or somewhat less than) the rate of formation of B. Equilibrium will then be unable to establish itself, since practically the whole of the substance B formed will be quickly converted into B'. The whole of the conversion of A into B' will then proceed as a reaction of the first order with a constant $q \leqslant k_1$. Since $k_1 = k_2 K_T$, therefore $q \leqslant k_2 K_T$, and hence $q \lll k_3 K_T$ (or $q \lll k_3' r K_T$).

We can reach the same conclusion on the basis of the full calculation for a system of two successive reactions of the first order, as carried out by Rakovsky, [18] if we take the fact that $k_2 \gg k_1$ into account*.

B) If the reaction $B \longrightarrow B'$ proceeds more slowly than $B \longrightarrow A$, then the actual concentration of B will approximate to its equilibrium value (it is equal, or almost equal, to its equilibrium value when k_3 is very small compared to k_2); we may therefore write:

$$b < c\,\frac{K_T}{1+K_T} = c\,\frac{k_1}{k_1+k_2} = \frac{k_1}{k_1+k_2}\,(c_0 - b').$$

The rate of formation of B' when the reaction $B \longrightarrow B'$ is a unimolecular one is therefore:

$$\frac{db'}{dt} < \frac{k_1k_3}{k_1+k_2}\,(c_0 - b')$$

or when it is bimolecular ($B + R \longrightarrow B'$):

$$\frac{db'}{dt} < \frac{k_1k_3'}{k_1+k_2}\,(c_0 - b')\,(r_0 - b').$$

In either case the process will proceed more slowly than the uni- or bimolecular reaction $A \longrightarrow B'$ would proceed for initial concentration c_0 (and r_0) and rate constants

$$q = \frac{k_1k_3}{k_1+k_2} \approx k_3K_T \text{ or } q' = \frac{k_1k_3'}{k_1+k_2} \approx k_3'K_T$$

Whatever the values of the rate constant k_3 or k_3' may be, therefore, the rate of the whole process, proceeding by the pseudomeric mechanism, is limited. The reaction always proceeds more slowly than the direct transformation $A \longrightarrow B'$ with initial concentration c_0 and constants $q = k_3K_T$ or $q' = k_3'K_T$.

In order to estimate the possible reaction rates of reactions having the pseudomeric mechanism, it is necessary to take into account that for pseudomeric equilibrium the value of K_T is always very small. The constants of many displaced tautomeric equilibria have now been determined: ethyl acetoacetate ($K_{T,\,H_2O} = 9.2 \cdot 10^{-4}$) [19], 4-quinolinol ($K_{T,\,H_2O} = 7.8 \cdot 10^{-5}$) [20], acetone ($K_{T,\,H_2O} = 2.5 \cdot 10^{-6}$) [21], nitromethane ($K_{T,\,H_2O} = 4 \cdot 10^{-8}$) [22]. All these, although displaced, are true tautomeric equilibria. By pseudomeric equilibria something different is understood, namely those equilibria in which the concentration of the form B is so low that it is quite impossible to determine the equilibrium constant by modern chemical and physical methods. The constants of pseudomeric equilibria must in any case be not higher than 10^{-10}, and probably of the order of $10^{-12}-10^{-15}$. The constant k_2 or k_3 must therefore be $10^{12}-10^{15}$

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* The differential equations for such reactions ($M_1 \rightleftarrows M_2 \longrightarrow M_3$) are:

$$\frac{dx_1}{dt} = k_1(a_1 - x_1) - k_2(a_2 + x_1 - x_2),$$

$$\frac{dx_2}{dt} = k_3(a_2 + x_1 - x_2)$$

(Rakovsky's notation), and they give on integration rather complex expressions for c_{M_1}, c_{M_2} and c_{M_3}, which, however, can be considerably simplified when $k_2 \gg k_1$. For the concentration c_{M_3} that is of interest to us (at time t), the exact expression

$$c_{M_3} = a_1 + a_2 + a_3 - \frac{c_1}{q_1}e^{-q_1t} - \frac{c_2}{q_2}e^{-q_2t}$$

for $k_2 \gg k_1$, $a_1 \gg a_2$ and $a_3 = 0$, becomes

$$c_{M_3} = a_1(1 - e^{-q_2t})$$

in which

$$q_2 = \frac{k_1+k_2+k_3}{2} - \frac{1}{2}\sqrt{(k_1+k_2+k_3)^2 - 4k_1k_3}.$$

The process therefore proceeds as a first-order reaction with an initial concentration of a_1 and a rate constant of q_2.

From the expression for q_2 it will be seen that $q_2 < k_1$, is always true. It follows that $q_2 < k_3K_T$, and since $k_3 \ll k_2$, we have finally that $q_2 \ll k_3K_T$.

times as great as the value of q, the rate constant of the unimolecular reaction, which must proceed more rapidly than the pseudomeric reaction under examination. In the same way, the constant k_3' must be $10^{12}-10^{15}$ times as great as q'.

The reactions to which the concept of pseudomerism is applied are not, however, slow reactions. All of them, on the contrary, are ordinary synthetic organic reactions, proceeding at the moderate speeds that are generally to be observed in laboratories. The numerical values of the unimolecular constants for these reactions lie in the range from $10^{-6}-10^{-4}$ sec^{-1} to $10-10^{2}$ sec^{-1}. In this case the constants k_2 and k_3 must have values of the order of greater than $10^{6}-10^{8}$, and probably than $10^{10}-10^{12}$ sec^{-1}. For the bimolecular constant k_3' values of the order of $10^{10}-10^{11}$ liter $mole^{-1}sec^{-1}$ and higher must also be assumed.

Rate constants of such an order are not, however, found for organic molecules. Even if such large values may be assumed for k_2 (the process $B \longrightarrow A$, for example, may be the ionization of the enol form and the subsequent recombination of ions to give the keto form), it is impossible to do so for k_3 or k_3'. It is well known that only ions or radicals (or atoms) are able to react with constants of the order of $10^{10}-10^{11}$ liter $mole^{-1}sec^{-1}$ at moderate temperatures (which correspond to a pseudounimolecular constant of the order of from $10^{8}-10^{9}$ to $10^{10}-10^{12}sec^{-1}$, depending on the concentration of the reagent present in excess (from 10^{-2} to 10 moles per $liter^{-1}$). The constants of the reactions of organic molecules are lower by many orders—all the more so for more complex molecules.

We therefore come to the conclusion that, if it is considered that the reaction proceeds by a pseudomeric mechanism, then it is necessary to assume high values for the constant k_3 or k_3' that cannot exist for organic molecules. If, however, we assume that the constant k_3 or k_3' has a possible (i.e. considerably lower) value, then it will be readily seen that pseudomeric reactions ought to proceed exceptionally slowly, which in fact they do not.[*]

We have carried out the calculation for the limiting case, when the equilibrium constant is of the order of $10^{-18}-10^{-15}$. Experiment, however, shows that also for considerably higher equilibrium constants, of the order of $10^{-6}-10^{-8}$ for example, the reaction does not proceed by the pseudomeric mechanism. We may take as an example the bromination of acetone or nitromethane, which proceeds not via the enol (aci) form, as was at one time thought, but as a result of the direct ionization of the keto (nitro) form.

We do not exclude, of course, the possibility of reaction with intermediate reversible formation of ions or radicals, the concentration of which may be very low, but which are capable of rapid reaction. In this case, however, we are not concerned with the question of pseudomeric equilibrium (of two isomeric organic molecules), but with the equilibrium of dissociation into ions or radicals. There is no question of pseudomerism here.

No place remains, therefore, for the pseudomerism concept. Introduced at the end of last century, when the technique available for the measurement of strongly displaced equilibria was still very poor and the information on the relative rates of chemical reactions was still very meager, it has persisted as an anachronism to the present day, thus greatly interfering with the development of concepts concerning the reactivity of tautomeric substances.

In the treatment of the mechanism of the formation of two series of derivatives by a substance that shows no signs of tautomerism, it is essential to abandon the concept of pseudomeric equilibria displaced to an immeasurably small extent as the cause of dual reactivity. If an equilibrium actually exists and is strongly displaced, for example, toward A, then it may be assumed, with confidence, that the derivative B' is formed not via B, but directly from A without the participation of B.

In the literature various suggestions have been made regarding the possible mechanism of the formation of the derivative B' directly from A without preliminary tautomerization. The old views of Michael [23] were based in such cases on the assumption that a molecule of the reagent (or its elements) adds to A and then splits away again in another order with formation of B'. Hückel criticized this concept [24]. Speculative hypotheses of various kinds have been made concerning such reactions on the basis of the "theory of resonance or mesomerism".

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[*] For example, when $K_T = 10^{-12}$ and $k_3 = 1$ (sec^{-1}), $q < 10^{-12}$ (sec^{-1}); when the half-period of the reaction is found to be $\tau \geqslant 20{,}000$ years. Even when $k_3 = 10^{4}$ sec^{-1}, i.e. for an unusually high rate constant, $\tau \geqslant 2$ years.

In this theory the basis of the explanation of the properties of substances is provided by a false idealistic concept of a multiplicity of molecular structures, each of which is only an imaginary form, but which, when taken together, determine, as a result of "resonance" "superposition", "excitation"), the structure and properties of the molecule. In spite of the fact that these "structures" do not give a representation of the real bonds in the molecule and have a speculative character, material reality has been ascribed to them: they "interact", and to this interaction the meaning of an objectively existing phenomenon "electronic resonance" is given; they "participate" in chemical reactions; they have "weight" and energy of "formation"; they are assigned definite chemical properties; and so on. The real molecule and its actual structure are replaced by fictitious concepts, and A. M. Butlerov's theory of chemical structure is replaced by a perverted theory.

The methodological invalidity and the physical untenability of the "theory of resonance or mesomerism" were exposed as a result of an extensive discussion in our scientific press and at the Conference on the Theory of Chemical Structure of June 11-14, 1951 [25]. One of the authors of the present paper, Kabachnik, has in the past expounded the "theory of resonance or mesomerism" in an uncritical fashion and has applied it for the explanation of the courses of chemical reactions: in a paper published in "Progress of Chemistry" in 1948 [26], for the explanation of orientation in the benzene ring; and in lectures given as an undergraduate in 1947. His subsequent work over a period of two years on the criticism of the "theory of resonance or mesomerism", in connection with the composition of an article by eight authors in "Progress of Chemistry" [27] and of a report to the Division of Chemical Sciences Committee [28], led the author to an appreciation of the highly erroneous nature of the "theory of resonance or mesomerism", of the completely illusory character of the explanations based on this theory, and of the invalidity of the above-mentioned paper in "Progress of Chemistry" and of the treatment given therein of the phenomenon of orientation in the benzene ring.

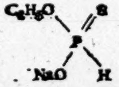
The explanations given on the basis of the "theory of resonance" of the formation of two series of derivatives from tautomeric and non-tautomeric substances, are tantamount to the "discovery" of a "resonance structure" responsible for a given series of derivatives. It is clear that such explanations are invalid.

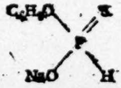
The authors consider that the actual explanation of the formation of two series of derivatives in absence of tautomerism, or under the conditions of very strongly displaced tautomeric equilibria, is to be sought in the concepts developed by Nesmeyanov of conjugation and transfer of reaction center [15]. The field previously assigned to pseudomerism is in actual fact the field of reactions that occur with transfer of reaction center.

III

The concepts developed above are confirmed by the properties of the dialkyl thiophosphites (I and II). They are colorless mobile liquids of characteristic odor. They dissolve in organic solvents and in aqueous alcohol, forming neutral solutions, but they are insoluble in water and in dilute aqueous caustic alkali. They are hydrolyzed by acids and alkalis with quantitative formation of phosphorous acid. They are oxidized by nitric acid, the reaction being very vigorous.

When dialkyl thiophosphites are treated with aqueous–alcoholic alkali, the alkali is gradually consumed, but it is found that the products are not the salts of (II), but sodium alkyl thiophosphites formed by the hydrolysis of one OR group:


(XV)


(XVI)

The consumption of alkali then slows down suddenly and to such an extent that dialkyl thiophosphites may be accurately, though slowly, titrated with alkali. These phenomena are similar to those observed by Nylen [29] for diethyl phosphite. Of the sodium alkyl thiophosphites (phosphonothionates) we have isolated (XV) and (XVI) in the pure state and analyzed them. The acid esters (RO)(HO)PSH, formed by acidification of solutions of these sodium salts with hydrochloric acid, are stable in aqueous solution and do not alter in titer in the course of a month. The relations that we have found indicate that dialkyl thiophosphites have the phosphonothionate structure (I), and not (II), since the form (II) should have strongly acidic properties. The insolubility of dialkyl thiophosphites in dilute alkalis indicates that if a tautomeric equilibrium (I)⇌(II) exists, then it is strongly displaced in the direction of (I) (concerning the hydrolysis of salts of dialkyl thiophosphites, see below).

The conclusion that dialkyl thiophosphites have the structure (I) is confirmed by the results of a determination of the molecular refractions of these compounds [3], as will be seen from Table 1.

TABLE 1

Molecular Refractions of Dialkyl Thiophosphites

Formula	Found MR_D	Calc. MR_D for $(RO)_2{=}P\begin{smallmatrix}S^*\\ H\end{smallmatrix}$	Calc. MR_D for $(RO)_2PSH^{**}$
$(CH_3O)_2PSH$	29.93	29.79	31.91
$(C_2H_5O)_2PSH$	38.91	39.02	41.15
$(C_3H_7O)_2PSH$	48.27	48.26	50.38
$(i\text{-}C_3H_7O)_2PSH$	48.64	48.26	50.38
$(C_4H_9O)_2PSH$	57.48	57.50	59.62

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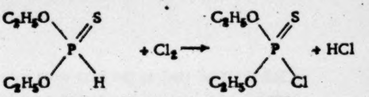
* P^V 4.27; S = 9.70.

** P^{III} 7.03; –S–9.06.

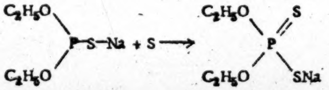
Confirmation of the formula (I) can be seen also in the inability that we have found in diethyl thiophosphite to unite with sulfur, cuprous halides, and alkyl halides. Diethyl thiophosphite is readily chlorinated in the cold with evolution of hydrogen chloride and formation of diethyl phosphorochloridothionate:


(I)   (XVII)

The analysis and constants of the product (XVII), which are identical with those given in the literature [30], leave no doubt concerning its structure.

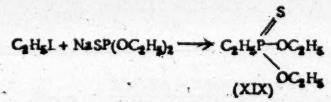
Diethyl thiophosphite, like diethyl phosphite, forms a sodium derivative: by the action of sodium on a benzene solution of diethyl thiophosphite (with evolution of hydrogen) or by the action of sodium ethoxide on diethyl thiophosphite in benzene or alcohol medium.

The sodium derivative of diethyl thiophosphite, unlike free diethyl thiophosphite, vigorously unites with sulfur at room temperature with formation of sodium O,O-diethyl phosphorothiolothionate. This property of the sodium derivative indicates the presence in its molecule of tervalent phosphorus and therefore a structure corresponding to the formula (V). The reaction with sulfur may accordingly be expressed by the equation:


(V)   (XVIII)

From the sodium O,O-diethyl phosphorothiolothionate obtained (XVIII) we have prepared the lead salt $[(C_2H_5O)_2PSS]_2Pb$, m.p. 75-76°. In admixture with authentic lead bis(O,O-diethyl phosphorothiolothionate) it showed no depression of melting point.

The sodium derivative of diethyl thiophosphite reacts in benzene or alcohol medium with alkyl halides, forming the corresponding esters of alkylphosphonothionic acids (i.e. not S- but P-derivatives):



$$C_2H_5I + NaSP(OC_2H_5)_2 \longrightarrow C_2H_5P(=S)(OC_2H_5)OC_2H_5$$

(XIX)

$$C_6H_5CH_2Cl + NaSP(OC_2H_5)_2 \longrightarrow C_6H_5CH_2PS(OC_2H_5)_2$$

(XX)

$$ClCH_2COOC_2H_5 + NaSP(OC_2H_5)_2 \longrightarrow C_2H_5OOCCH_2PS(OC_2H_5)_2$$

(XXI)

The alkylphosphonothionic esters obtained (XIX and XXI), on being hydrolyzed in sealed tubes with hydrochloric acid, give ethyl chloride and hydrogen sulfide and are converted into the corresponding known phosphonic acids (XXII) and (XXIII) [31,32].

$$C_2H_5PO(OH)_2 \qquad\qquad HOOC{-}CH_2PO(OH)_2$$

(XXII) (XXIII)

Diethyl ethylphosphonothionate (XIX), since it contains a P═S bond, should be capable of undergoing Pishchimuka's rearrangement [33]. Actually, when diethyl ethylphosphonothionate (XIX) is heated with ethyl iodide, an isomeric compound, of higher boiling point, specific gravity, and refractive index, is formed. This change in constants is quite characteristic for Pishchimuka's rearrangement:

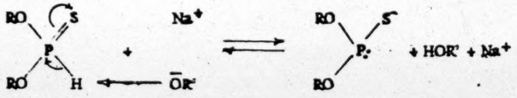
$$C_2H_5PS(OC_2H_5)_2 \xrightarrow{C_2H_5I} C_2H_5PO(SC_2H_5)(OC_2H_5)$$

(XXIV)

On the basis of the reactions of dialkyl thiophosphites that we have studied, it may be regarded as established that they have the structure (I). Equally, we may consider the structure (V) to be established for the sodium derivative of diethyl phosphite. Finally, there can be no doubt that the products of alkylation with alkyl halides have the structures (XIX–XXI), i.e. are esters of alkylphosphonothionates containing a quinquevalent phosphorus atom. The fact that the free dialkyl thiophosphites have the structure (I) and are insoluble in dilute aqueous alkalis, but in nonaqueous media with alkoxides or sodium form metal derivatives that are readily hydrolyzed by water, undoubtedly indicates the presence of tautomerism (I) $\rightleftharpoons$ (II) the equilibrium being strongly displaced in the direction of (I). If the equilibrium did not exist, then the hydrolysis in aqueous solution of the salts of the acid (II), which should be a fairly strong acid (in any case, not weaker than the thiols), would occur only to an insignificant extent. If, on the contrary, there exists an equilibrium between two acids, one of which is a very weak acid, then it is easy to show that the hydrolysis of a salt of such a pair of acids will proceed as if it were the hydrolysis of the salt of the weaker acid.*

The fact that free dialkyl thiophosphites did not enter into addition reactions (with sulfur, for example) we explain by the low effective concentration of the form containing tervalent phosphorus (II) (hence extreme slowness of reaction).

It may be supposed that the formation of a sodium derivative from (I) proceeds with transfer of reaction center:



Transfer of reaction center evidently occurs also in the alkylation with alkyl halides of the sodium derivative of dialkyl thiophosphite, irrespective of whether this reacts as an undissociated molecule:

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* The hydrolysis constant for the salt of an equilibrium pair of acids (I) and (II):

$$K_{hydr.} = \frac{(c_I + c_{II})\, c_{OH^-}}{c_{A^-}}$$

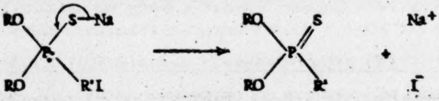
may be expressed in terms of the ionization constants of the forms K'_I and K'_{II}:

$$K_{hydr.} = \frac{K_W\,(K'_I + K'_{II})}{K'_I K'_{II}}$$

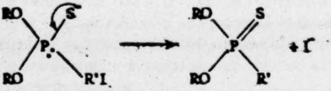
(K_W is the ionic product for water). When K'_I is very small in comparison with K'_{II}, it may be neglected in the numerator, and we obtain:

$$K_{hydr.} = \frac{K_W}{K'_I}.$$

The hydrolysis of a salt of tautomeric acids proceeds, therefore, as the hydrolysis of a salt of the less acidic form.



or as the anion:



All the properties found for dialkyl thiophosphites may therefore be explained without the introduction of unfounded concepts of pseudomerism or of resonance (mesomerism).

EXPERIMENTAL

Hydrolysis of Dialkyl "Thiophosphites"

1) A weighed amount of the substance was dissolved in aqueous alcohol (1:1) and slowly titrated with 0.1 N NaOH with phenolphthalein as indicator. The disappearance of the pink color was at first fairly rapid, but became slower and slower, so that toward the end of the titration 5-8 minutes were required for the disappearance of the color due to 2-3 drops of alkali. Diisopropyl thiophosphite was hydrolyzed exceptionally slowly. The results are given in Table 2.

TABLE 2

Equivalent Weight (Hydrolysis of One OR-Group)

Formula	Found	Calculated
$(CH_3O)_2PSH$	127.3; 127.5	126
$(C_2H_5O)_2PSH$	153.0; 153.4	154
$(C_3H_7O)_2PSH$	184.2; 184.0	182
$(C_4H_9O)_2PSH$	210.9; 210.3	210

2) Diethyl thiophosphite (0.9417 g) was dissolved in aqueous alcohol (3:2; 50 ml) and slowly titrated until neutral to phenolphthalein. The volume of 0.1 N NaOH (factor, 1.000) required was 61.08 ml (corresponding to an equivalent weight of 154.2, the calculated value being 154). An immediate addition of 61.08 ml of 0.1 N HCl (factor, 1.000) was made, and it was found that the titer of the solution did not change in the course of one month.

Preparation of Sodium Ethyl Thiophosphite (Phosphonothionate) (XV). Diethyl thiophosphite (1.54 g) was dissolved in alcohol (3 ml) and water (2 ml), and the solution was mixed with a solution of NaOH (0.40 g) in water (3 ml). The alkaline reaction gradually disappeared. The solvent was evaporated over phosphoric oxide in a desiccator, and the salt that remained was washed with ether and dried, yielding very hygroscopic colorless leaves.

Found %: P 20.78; 20.63

$C_2H_6O_2PSNa$. Calculated %: P 20.95

Preparation of Sodium Butyl Thiophosphite (Phosphonothionate) (XVI). This was prepared in a similar way from 6.3 g of dibutyl thiophosphite and 1.20 g of NaOH. The yield of sodium butyl thiophosphite was 5 g (colorless soft scales).

Found %: P 17.37; 17.12

$C_4H_{10}O_2PSNa$. Calculated %: P 17.61

Action of Sulfur on Diethyl Thiophosphite

A mixture of 15.4 g of diethyl thiophosphite and 3.2 g of sulfur was heated in a water bath for five hours, cooled, and filtered to remove excess of sulfur (3 g). The substance was vacuum-distilled. It had b.p. 64-66°/12 mm and n_D^{20} 1.4586; pure $(C_2H_5O)_2PSH$ has b.p. 67.5-68.5°/12 mm and n_D^{20} 1.4597.

Preparation of Diethyl Phosphorochloridothionate (XVII)

Dry chlorine was passed into diethyl thiophosphite (11.6 g) cooled to −10° until the weight had increased by 5.4 g; hydrogen chloride was evolved. The chlorination product was vacuum-fractionated twice. The fractions obtained at 12 mm were: Fraction I, b.p. 57-81°, 2.8 g; Fraction II, b.p. 81-82°, 6.3 g (45 %). n_D^{20} 1.4711; d_4^{20} 1.1918.

Found %: Cl 18.57; 18.25; S 16.74; 16.53; P 16.40; 16.51

$C_4H_{10}O_2PSCl$. Calculated %: Cl 18.83; S 16.98; P 16.45

For Fletcher and coworkers [30] give b.p. 71.5-72°/7 mm and 94-96°/20 mm, n_D^{20} 1.4685. A preparation obtained by us exactly according to Fletcher's instructions had b.p. 90.5-91.5°/19 mm, d_4^{20} 1.1899; n_D^{20} 1.4705.

Preparation of Sodium O,O-Diethyl Phosphorothiite (V)

The sodium derivative of diethyl thiophosphite was prepared by the action of finely divided sodium on diethyl thiophosphite in a medium of benzene. There was an abundant liberation of hydrogen, and the sodium derivative separated as a voluminous finely crystalline colorless precipitate. The following method of preparation was found to be preferable: sodium ethoxide was prepared in benzene medium from finely divided sodium and an equivalent amount of alcohol, and the calculated amount of diethyl thiophosphite was then added. Finally, it is possible to add diethyl thiophosphite to an alcoholic solution of sodium ethoxide, but the sodium O,O-diethyl phosphorothiite then remains in solution.

The silver derivative of diethyl thiophosphite was prepared by addition of an equivalent amount of aqueous silver nitrate solution and several drops of ammonia to an alcoholic solution of diethyl thiophosphite; it formed a white precipitate that rapidly darkened in color. It dissolved slowly in benzene with formation of a silver sol.

Reaction of Sodium O,O-Diethyl Phosphorothiite with Sulfur

The sodium derivative was prepared in benzene (12 ml) from diethyl thiophosphite (4.62 g) and sodium (0.69 g). After a short heating and then cooling, flowers of sulfur (0.96 g) were added. The liquid was heated at the boil, and the sulfur dissolved. After one hour the small amount of precipitate was filtered off and the substance was extracted from solution with water. To the aqueous extract a saturated solution of basic lead acetate was added. A colorless lead salt (6.9 g), m.p. 74-75.5°, was obtained. The recrystallized product (6.1 g, from alcohol) melted at 75-76°. In admixture with authentic lead salt $[(C_2H_5O)_2PSS]_2Pb$, it melted at 74.5-75.5°.

Preparation of Esters of Alkylphosphonothionic Acids

Reaction of Sodium O,O-Diethyl Phosphorothiite with Ethyl Iodide. Ethyl iodide (22.8 g) was added slowly to the sodium derivative prepared from diethyl thiophosphite (23.1 g) and sodium (3.44 g) in a benzene medium. The mixture was set aside until it ceased to have an alkaline reaction (four days). The precipitate of sodium iodide was washed out with water, and the benzene solution was dried over sodium sulfate. After three vacuum fractionations, the following fractions were obtained at 13.5 mm: Fraction I, b.p. 72-82°, 2.3 g; Fraction II, b.p. 82-83.5°, 13.7 g (50%); d_4^{20} 1.0332; n_D^{20} 1.4563.

Found %: C 39.66; 39.68; H 8.17; 8.13
$C_6H_{15}O_2SP$. Calculated %: C 39.56; H 8.24

Diethyl ethylphosphonothionate (XIX) is a colorless liquid, soluble in organic solvents and insoluble in water. It is very difficult to hydrolyze; it does not contain P^{III}.

Reaction of Sodium O,O-Diethyl Phosphorothiite with Ethyl Chloride. This was performed as in the preceding experiment. The product from 11.6 g of diethyl thiophosphite, 1.72 g of sodium, and excess of ethyl chloride was 6.1 g (46.5%) of a substance of b.p. 90-93.5°/19 mm, n_D^{20} 1.4545; d_4^{20} 1.0324.

Hydrolysis of Diethyl Ethylphosphonothionate. The substance (XIX) (4 g) was heated with double its volume of hydrochloric acid (1:1) in a sealed tube for three hours at 145-155°. When the tube was opened, the presence of a small pressure of ethyl chloride was revealed. The aqueous solution was evaporated to dryness, and the residue crystallized out when allowed to stand over phosphoric oxide. The crystals were pressed out on a plate and recrystallized from water (by evaporation of the solvent); m.p. 57-58°.

Found %: P 27.82; 27.82
$C_2H_7PO_3$. Calculated %: P 28.18

For ethylphosphonic acid the literature gives m.p. 60.5-61.5° [31]. Ethylphosphonic acid that we prepared by the reaction of Michaelis and Becker melted at 60°, and a mixture of the two preparations at 58-59°.

Preparation of Diethyl Ethylphosphonothiolate (XXIV). Diethyl ethylphosphonothionate (XIX) (4 g) was heated in a sealed tube with an equal volume of ethyl iodide at 140-150° for three hours. A large amount of $(C_2H_5)_3SI$ crystals were formed in the tube. The liquid was poured from the crystals and was vacuum-fractionated twice, yielding 1.3 g of diethyl ethylphosphonothiolate, b.p. 76-76.5°/4 mm, d_4^{23} 1.0709; n_D^{20} 1.4730.

Found %: C 39.93; 40.08; H 8.25; 7.98; P 17.15; 16.97

$C_6H_{15}O_2SP$. Calculated %: C 39.56; H 8.24; P 17.03

Preparation of Diethyl Benzylphosphonothionate (XX). To sodium O,O-diethyl phosphorothiite prepared in benzene from 7.7 g of diethyl thiophosphite and 1.15 g of sodium, benzyl chloride (6.82 g) was added. Vigorous reaction accompanied by boiling set in. After two days a test of the reaction mixture showed it to be neutral, and the benzene solution was washed with water, dried over sodium sulfate, and vacuum-fractionated. The fraction (5.3 g) of b.p. 124-125°/3.5 mm was separated; it had d_4^{20} 1.1022; n_D^{20} 1.5303.

Found %: P 12.55; 12.62

$C_{11}H_{17}O_2PS$. Calculated %: P 12.70

The substance was a colorless liquid, insoluble in water. After hydrolysis it gave no reaction for P^{III}.

Preparation of Diethyl Ethoxycarbonylmethylphosphonothionate (XXI). Diethyl ethoxycarbonylmethylphosphonothionate was prepared in a similar way from 11.6 g of diethyl thiophosphite, 1.72 g of sodium, and 9.2 g of chloroacetic acid. Two distillations yielded 13.0 g (72.2%) of a substance having b.p. 105-106°/5 mm, d_4^{20} 1.1204; n_D^{20} 1.4621.

Found %: C 40.47; 40.43; H 7.05; 6.96; P 12.69; 12.87

$C_8H_{17}O_4PS$. Calculated %: C 40.00; H 7.12; P 12.96

Diethyl ethoxycarbonylmethylphosphonothionate is a colorless liquid, insoluble in water. It is difficult to hydrolyze, and after hydrolysis it gives no reaction for P^{III}.

Hydrolysis of Diethyl Ethoxycarbonylmethylphosphonothionate. The ester (XXI) (2 g) was heated in a sealed tube with HCl (1:1) at 130° for three hours. There was a pressure in the tube when it was opened. The contents were evaporated on a water bath and were evaporated down several times with water in order to remove HCl. The residue crystallized out on standing. The melting point was 138-139°; for carboxymethylphosphonic acid the literature gives 139.5° [34].

SUMMARY

1. The question of pseudomerism has been examined. It has been shown that the concept of pseudomerism demands the assumption of abnormal rates of reaction for organic molecules. The concept of pseudomerism is invalid.

2. It has been suggested that the reactions previously assigned to the field of pseudomerism proceed in fact with transfer of reaction center in the manner indicated by Nesmeyanov, without preliminary tautomeric change.

3. The paper "Orientation in the Benzene Ring", published in "Progress of Chemistry" by one of the authors, Kabachnik, was unsound. The author then adopted the "theory of resonance or mesomerism" in an uncritical fashion, expounded it, and applied it in the explanation of chemical reactions. The author is now thoroughly convinced of the methodological unsoundness and physical invalidity of the "theory of resonance or mesomerism" and regards all explanations of chemical phenomena made on the basis of this "theory" as illusory.

4. The properties of dialkyl thiophosphites have been investigated. It has been shown that the structure of the free dialkyl thiophosphites corresponds to the phosphonothionate formula, in which the phosphorus atom is quinquevalent. The tautomeric equilibrium of dialkyl thiophosphites in solution is very strongly displaced in the direction of the quinquevalent form.

5. It has been shown that dialkyl thiophosphites are able to form metal derivatives containing tervalent phosphorus (phosphorothiites). Alkylation of these yields esters of alkylphosphonothionic acids.

6. It has been suggested that the formation of the sodium derivatives of dialkyl thiophosphites and their alkylation proceed with transfer of reaction center in the manner indicated by Nesmeyanov.

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BRIEF COMMUNICATIONS

RAMAN SPECTRA OF TWO SILAHYDROCARBONS

M. V. Volkenshtein and E. I. Pokrovsky

We have determined the Raman spectra of triethyl (2-methylpropenyl) silane and diallylmethylsilane. As these spectra have not been published previously, we give here the results we have obtained.

Triethyl(2-methylpropenyl)silane $(C_2H_5)_3SiCH_2C(CH_3)=CH_2$ has b.p. 188.5°/750 mm; n_D^{20} 1.4505; d_D^{20} 0.7994. Its spectrum contains the following lines (frequencies in cm^{-1}, visually assessed degree of blackening in parentheses): 142(1), 294(1), 424(1), 490(2), 561(4), 630(1), 964(3), 1013(0), 1042(0), 1107(6), 1127(3), 1173(2), 1228(2), 1297(2), 1371(0), 1409(1), 1459(2), 1630(3), 2783(10), 2880(3), 2910(2), 2956(1), 3081(1), 3130(4).

Frequencies in the range 2783-3130 correspond to valency vibrations of C−H bonds; in range 1371-1459, to deformation vibrations of HCH; 1630 cm^{-1} corresponds to valency vibration of C=C; and frequencies in range 900-1100 correspond to valency vibrations of C−C bonds.

Tetramethylsilane has the frequencies: 202(20), 239(15), 598(20), 696(15), 863(10), 1264(10), 1427(15), 2905(10), 2963(10) [1]. Tetraethylsilane has the frequencies 160(4), 249(3), 303(6), 393 (2), 553(10), 625 (3), 736(3), 865(1), 978(5), 1021(5), 1200(7), 1423(7), 1467 (8), 2734(1), 2813(3), 2885(10), 2912(6), 2950(5) [2].

Comparison of the spectra shows that frequencies 142(1) and 294(1) related to deformation vibrations of C−Si−C, and the frequency 561(4) to the valency symmetrical vibration of the group $Si(CH_2-)_4$.

Diallylmethylsilane $CH_3HSi(CH_2CH=CH_2)_2$ has the b.p. 122.5°/745 mm, n_D^{20} 1.4662; d_4^{20} 0.8055. The spectra contains the following lines: 353(1), 406(3), 556(5), 893(2), 929(1), 983(1), 1116(1), 1153(10), 1190(3), 1234(2), 1296(6), 1392(3), 1493(2), 1627(8), 2117(3), 2601(2), 2900(2), 2972(1), 2997(3), 3087 (2).

The C−H, HCH, C=C, and C−C frequencies lie in the same ranges. The frequency 556(5) corresponds to a valency semisymmetrical vibration of $-Si(CH_3)(CH_2-)_3$. The frequency 2117(3) is the valency vibration of the Si−H bond (in SiH_4 2183 cm^{-1}, and in Cl_3SiH 2257 cm^{-1}).

The substances were synthesized by V. F. Mironov in A. D. Petrov's laboratory [3]. We are indebted to A. D. Petrov for providing these substances.

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CHRONICLE

SCIENTIFIC AND TECHNICAL SESSION ON ION EXCHANGE

A Scientific and Technical Session on Ion Exchange was held in Moscow from 3rd to 6th of June, 1952; the meeting was called jointly by the High-parameter Steam Committee of the Energetics Research Institute of the USSR Academy of Sciences, by the Institute of Physical Chemistry of the USSR Academy of Sciences, and by the Institute of Macromolecular Compounds of the USSR Academy of Sciences. Active part in the work of the Session was taken by institutes of the USSR Academy of Sciences (Institutes of Physical Chemistry and of Macromolecular Compounds, and V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry), the Institute of Organic Chemistry of UkrSSR Academy of Sciences, specialist institutes (L. Ya. Karpov Institute of Physical Chemistry, All-union Thermotechnical Institute, Institute of Pure Chemical Reagents, Central Institute of the Sugar Industry, All-union Research Institute of the Hydrolysis Industry, Institute of the Nickel and Tin Industry, Leningrad Medical and Pediatric Institute, OTB), and higher education establishments (A. A. Zhdanov Leningrad State University, Kharkov State University, D. I. Mendeleev Moscow Institute of Chemical Technology, Timiryazev Agricultural Academy, Moscow Institute of Chemical Pharmaceutics). Four main questions were discussed at the Session: a) the theory of ion exchange; b) the synthesis of ion-exchange materials; c) the investigation and testing of ion-exchange materials; and d) the application of ion-exchange materials. About forty papers were read at the Session.

In his introductory address the chairman of the organizing committee, Prof. K. B. Chmutov, Doc. Chem. Sci., reported on the implementation of the decisions taken at the conference on chromatography in 1950, gave a brief review of the state of scientific knowledge on the main questions in the program of the Session, and pointed out the most important items, which would require detailed examination. The speaker emphasized that the whole program of the Session was essentially pervaded by chromatography, the method developed by the remarkable Russian scientist M. S. Tsvet and applied in one form or another in all the scientific establishments of the country. Chmutov emphasized also that all the questions to be discussed at the Session represented the further successful development of outstanding work by the Russian scientistis K. K. Gedroits, H. A. Shilov, E. N. Gapon, and B. P. Nikolsky. Even a brief exposition of the contents of each of the numerous papers would require much space. We shall therefore examine only the more important results on the fundamental questions discussed at the Session.

a) Theory of Ion Exchange. The following papers were presented in this part of the Session: K. M. Saldadze, Cand. Tech. Sci., (IREA) "Quantitative Laws determining the Ion-exchange Process"; V. V. Rachinsky, Cand. Phys. Math. Sci., (Timiryazev Agric. Acad.) "Present State of Ion-exchange Chromatography"; N. N. Tunitsky, Doc. Chem. Sci., (L. Ya. Karpov Institute) "Theory of the Elution of Chromatographic Bands"; A. T. Davydov, Cand. Chem. Sci., (Kharkov State Univ.) "Laws of Ion Exchange on Soviet-produced Ionites"; M. Ya. Romankevich, Cand. Tech. Sci., (Inst. Org. Chem. Acad. Sci. Ukr SSR) "Diffusion Processes in Ion Exchange". The investigations reported at the Session showed that ion exchange on organic ion-exchange materials is a heterogeneous chemical reaction that may be described by the mass action law. At the same time it is necessary to remember that, in addition to the ion-exchange reaction, side reactions, such as hydrolysis, complex formation, reduction, oxidation, etc., may also occur on cationites and anionites. The process of ion exchange under static conditions is most fully described by the equations proposed by B. P. Nikolsky and E. N. Gapon. Prof. O. I. Ryabchikov and M. M. Senyavina, Cand. Chem. Sci., (GEOKhI, Acad. Sci. USSR) criticized work by American authors on the mechanism of ion-exchange chromatography in which complex-formers are used, and they reported the results of experimental investigations on the establishment of the nature of the complex compounds and of the relationship between the efficiency of the experiment and the pH of the medium and the concentration of complex-former.

From the discussion of material on the kinetics of ion-exchange processes it was possible to conclude that the kinetics are of a diffusion character. Much interest was aroused by the paper of M. Ya. Romankevich on a new method of measuring diffusion coefficients in an ion-exchange material. In this method diffusion processes are studied in plates of the ion-exchange material. Diffusion coefficients determined by this method are of the same order as those found by the dynamic method (see Prof. N. N. Tunitsky's paper). In a number of papers material was presented which illustrated qualitatively the direct relation of the swelling propensity of cationites to the kinetic process of ion exchange.

The Session found that in the dynamics of ion exchange there was at present no theory covering the whole complex of questions involved. Two approaches to the solution of this problem were noted. V. V. Rachinsky, Cand. Phys. Math. Sci., (Timiryazev Agric. Acad.) together with T. B. Gapon, Cand. Chem. Sci., (Inst. Phys. Chem.) are working along the lines developed by Prof. E. N. Gapon: the dynamics of ion exchange are treated on the basis of the laws of statics, kinetic factors being considered to play a secondary part. Prof. N. N. Tunitsky and E. L. Cherneva, Cand. Chem. Sci., (L. Ya. Karpov Institute), in developing the dynamics of ion exchange, take the kinetics of the process into account; they treat the dynamics of chromatography in general and do not particularize the theory for the case of ion exchange.

b) Synthesis of Ion-exchange Materials. The magnitude of the contribution in papers to this section bore witness to the hard, fruitful work of Soviet workers on the synthesis of high-quality ion-exchange materials. In particular, papers were read at the session by representatives of the Institute of Macromolecular Compounds of the USSR Academy of Sciences, the State Inst. of Applied Chem., the OTB, the Mendeleev Moscow Inst. of Chem. Tech. Departments of Macromolecular Compounds and of Plastics Technology), and the Frunze Plastics Research Institute. The Session noted that owing to the efforts of a considerable number of organizations the question of the synthesis of home-produced high-quality cationites and anionites must be regarded as solved; nevertheless, commercial production of the brands synthesized by the institutes is somewhat behind schedule in a number of instances. The Session noted also the need for organizing the sale of ion-exchange materials required for chemical analysis in small packages (in the same way as chemical reagents).

c) Investigation and Testing of Ion-exchange Materials. On this subject the following papers were read at the Session: Prof. D. I. Ryabchikov and M. M. Senyavin, Cand. Chem. Sci., (GEOKhI) "Comparative Study of Certain Ion-exchange Materials"; E. A. Materova, Cand. Chem. Sci., and V. I. Paramonova, Cand. Chem. Sci., (Leningrad State Univ.) "Physicochemical Characteristics of Ionites"; T. B. Gapon, Cand. Chem. Sci., (Inst. Phys. Chem.) "Investigation of the Physicochemical Properties of Ion-exchange Resins with a View to Their Grading and Classification"; Prof. A. A. Vanshteidt, A. A. Vasilyev, Cand. Tech. Sci., and O. I. Okhrimenko, Cand. Tech. Sci., (Inst. Macromol. Comp.) "Titrimetric Method for the Quantitative Determination of Sulfo and Carboxyl groups in Cationites". In these papers the exchange capacity of ionites received the fullest characterization, and in the choice of indexes the speakers based their considerations on the fundamental postulates of the theory of ion exchange. It was shown that it is desirable to determine the total exchange capacity (by the method of potentiometric titration of weighed portions) and the exchange capacity under dynamic conditions; the first index expresses the total exchange capacity under static conditions for all values of the pH of the medium, and the second permits us to estimate the selective action of the sample under investigation and to establish the kinetic properties of the ion-exchange material. Detailed study of a large number of Soviet and foreign ion-exchange materials shows that a number of Soviet cationites and anionites are superior in quality to the best foreign samples. The session gave great attention to the question of a single standard procedure for the testing of ion-exchange materials: one which would permit a sufficiently complete characterization of industrial cationites and anionites by the aid of comparatively few determinations and would enable comparative evaluations of samples to be made. Owing to the great variety of the demands made on ion-exchange materials by different users, the Session recommended all organizations using ionites to let the Chromatography Committee know their specific requirements in order to provide a basis for the coordination of work on the establishment of a single standard method of test.

The question of the investigation of ion-exchange materials was considered by F. G. Prokhorov, Cand. Tech. Chem., All-union Thermotechnical Institute, in his paper on "Ionite Materials and the Problem of Chemical Desalting of Natural Waters and Condensates" and by O. N. Grigorov, Cand. Chem. Sci., and I. V. Volf in their paper on "Sulfonated Ion-exchange Adsorbents from Humic Substances". Prokhorov gave some very interesting data on the "aging" of anionites when preserved or used for a long time; as Prokhorov's work shows, "aging" of anionites occurs as a result of their oxidation, which causes amphoteric properties to appear in anionites and leads to an appreciable reduction in exchange capacity.

d) Application of Ion-exchange Materials. A fair number of papers was devoted to this question. We will mention the following: S. M. Chemobrov, Cand. Tech. Sci., (Institute of the Nickel Industry) "Exchange of Nickel Ions on Cationites"; A. B. Davankov (Lecturer, Moscow Inst. Chem. Tech.) "Extraction of Phenol from Aqueous Solutions by Anionite Resins"; Prof. F. M. Shemyakin (Pharmaceutical Institute) "Use of Soviet Ionite Materials in Chemical Analysis"; Prof. L. T. Solovyev (Leningrad Pediatric Institute) "Separation of Mixtures of [illegible]

[illegible]

of Amino Acids by Ion-exchange Adsorption in Columns of Synthetic Resins"; G. S. Benin, Cand. Tech. Sci., (Sugar Research Institute) "Application of Ionites in the Sugar Industry"; M. Ya. Romankevich, Cand. Tech. Sci., (Inst. Org. Chem., UkrSSR Acad. Sci.) "Partial Purification of Sugar Juices by Cationites"; Itenberg, Cand. Tech. Sci. (Novosibirsk Plastics Factory) "Experience Gained in the Use of an Industrial Plant for the Demineralization of Water with Ion-exchange Resins"; B. O. Lyubin, Cand. Tech. Sci., (All-union Research Institute for the Hydrolysis Industry) "Application of Organic Ionites in the Hydrolysis Industry"; a number of papers were devoted to the application of ion-exchange materials in fine chemical technology and in the medicinal industry, also to the technical perfection of the chromatographic process. In its resolutions the Session pointed out the need for increasing the range of commercial ion-exchange materials and for reducing their cost, thus widening the field of application of ionites; the Session pointed out also the desirability of developing standard ion-exchange apparatus.

Concrete resolutions were passed on all of the questions considered. These pointed out the direction that must be taken in the further development of the study and application of ion-exchange processes and ion-exchange chromatography. In its general recommendations the Session emphasized the need for setting up a committee on chromatography attached to the USSR Academy of Sciences, for training specialist teams for work on ion exchange and chromatography in the higher eduction establishments for the study of chemistry, and for the systematic publication of work in journals, collections of articles, and monographs.

The overburdening of the agenda with papers and the absence of sectional meetings reduced the possibility of holding a wide discussion, and this was one of the main faults in the organization of the Session. Note should be taken also of the insufficiently wide notification of workers in institutes and industry of the convening of the session and of the nature of its program.

JOINT SCIENTIFIC SESSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE USSR ACADEMY OF SCIENCES AND THE ACADEMY OF SCIENCES OF THE UZBEK SSR

On October 24-29, 1952 a Visiting Scientific Session of the Division of Chemical Sciences of the USSR Academy of Sciences was held in Tashkent jointly with the UzbekSSR Academy of Sciences.

The Session assembled in the atmosphere created by the new powerful uplift experienced by the Soviet people, both politically and with respect to production, as a result of the appearance of Comrade Stalin's great work "Economic Problems of Socialism in the USSR" and the resolutions passed by the Nineteenth Congress of the Communist Party of the Soviet Union. The main problems before the Session were the coordination of investigations of workers on chemical questions connected with solution of scientific and economic problems of immediate importance for Uzbekistan and the consideration of the present state and possible further development of these investigations. Considerable attention was devoted to the problem, very important for the national economy of Uzbekistan and of the whole Soviet Union, of the growing of cotton. During the Session, therefore, special conferences were held on the chemistry of mineral fertilizers and on the chemistry and physical chemistry of the cotton fiber.

Considerable importance was attached to personal contacts between scientists, and a beginning was made in this direction in the course of the inspection of the laboratories of the Institute of Chemistry of the Uzbek SSR Academy of Sciences, which was carried out on the the opening day of the Session. Joint discussions began on concrete questions connected with experimental problems facing the chemists of Uzbekistan.

The first meeting of the Joint Scientific Session took place on October 24th in the Sverdlov Concert Hall. Participants in the meetings of the session were members of the Division of Chemical Sciences of the USSR Academy of Sciences, scientific workers of the Institute of Chemistry and other scientific organizations of the UzbekSSR Academy of Sciences, of the Central Asian State University, of the Tashkent Polytechnical Institute, of the UzbekSSR Agricultural Institute, of the Tashkent Textile Institute, and of the Cotton Research Institute, and representatives of the chemical institutes of the Academies of Sciences of the Uzbek, Kazakh and Turkmen republics and of the Kirgiz affiliated institute of the USSR Academy of Sciences; also technologists of industrial undertakings of the Uzbek SSR and teachers from higher education establishments.

The Session was opened by T. Z. Zakhidov, president of the Uzbek SSR Academy of Sciences. In greeting the participants on behalf of the Presidium of the Uzbekistan Academy of Sciences and the scientists of the Uzbek SSR, T. Z. Zakhidov said that this Session heralded a new stage in the establishment of yet closer scientific and creative cooperation of chemists and representatives of the Uzbekistan chemical industry with other scientists of our great Fatherland.

Iosif Vissarionovich Stalin's great work "Economic Problems of Socialism in the USSR", the historic resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union, and the speechof Comrade Stalin at the Nineteenth Party Congress directed to us Soviet scientists — these form the lodestar in our journey to the solution of the urgent problems of building communism and in the further progress of our advanced Soviet science.

In an exposition of the fundamental problems confronting Uzbekistan chemists, T. Z. Zakhidov said that he was sure that the present Session would subject the work of the chemists to critical analysis by means of an extensive exchange of opinions and constructive criticism, that it would consider in a business-like way the vital problems facing Uzbekistan scientists, and would pave the way for a powerful thrust forward in the study of the chemistry of cotton and in the further development of inorganic, organic, and physical chemistry. T. Z. Zakhidov ended his speech by proposing a toast in honor of the banner-bearer of peace, the eminent man of science, Iosif Vissarionovich Stalin.

Hearty applause greeted the election as Honorary Presidium of the Presidium of the Central Committee of the Communist Party of the Soviet Union, with the great I. V. Stalin, leader of the workers and eminent men of science, at its head.

The chairman at the first meeting, Academician-Secretary of the Division of Chemical Sciences of the USSR Academy of Sciences, M. M. Dubinin, on behalf of the participants in the Session, expressed hearty thanks to the Presidium of the Uzbek SSR Academy of Sciences, to the Bureau of the Division of Technical and Geologo-Chemical Sciences, and to the whole community in Uzbekistan for the great amount of work they had put into the organization of the present Session; he expressed his confidence in the success of the work of the Session.

The Joint Session was taking place in a year that had acquired a historic significance in the life of the peoples of the Soviet Union. Two events of enormous importance were associated with this historic year: the appearance of I. V. Stalin's great work "Economic Problems of Socialism in the USSR", and the holding of the Nineteenth Congress of the Communist Party of the Soviet Union.

After giving a brief exposition of the work of Honorary Academician I. V. Stalin and of the directives of the CPSS Congress on the growth of production of the most important chemical products, M. M. Dubinin considered the honorable tasks allotted to Soviet scientists in the report rendered by Comrade Malenkov: "to develop further our advanced Soviet science with the object of occupying the first place in world science; to direct the efforts of scientists to the more rapid solution of the problems involved in the utilization of the enormous natural resources our country; and to strengthen the creative cooperation of science with production, remembering that this cooperation enriches science with experience from practice and helps practical workers to solve their problems more rapidly"*, and he expressed his assurance that Soviet chemists would carry out with honor the historic tasks presented to them by the resolutions of the Nineteenth Congress of the Comunist Party.

The first paper to be heard was that of I. S. Kantsepolsky, Cand. Chem. Sci., on the subject of "Hydrotechnical Cements in the Central Asian Republics". The speaker described investigations on local naturally (gliezh) and artificially (glinite) burnt clays, which were found to be the most suitable additions for the pozzolanization of Portland cement. It has been shown possible to obtain sulfate-stable cements based on Portland cement and glinite.

The pozzolanic Portland cement having 30% of gliezh which is produced at present in Uzbekistan, although it has a higher water and sulfate-stability than Portland cement, is not as good as sulfate-stable pozzolanic Portland cement prepared with additions of tripolite. The speaker had set himself the task of increasing the sulfate-stability of gliezh Portland cement by changing the mineralogical composition of the cement clinker. Cements have been produced under manufacturing conditions that satisfy the technical requirements for high-quality Portland cements. Addition of gliezh greatly increased the sulfate-stability of Portland cement. Pozzolanic Portland cement containing 50% of gliezh, prepared on the basis of cement clinker, was not subject to sulfate aggression. It has been shown requirements of the constructors of the Main Turkman Canal for use in different zones of the canal.

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* G. Malenkov, Report rendered to the Nineteenth Congress of the Party on the work of the Central Committee of the All-Union Communist Party (bolsheviks), "Pravda" Press, 1952, p. 62.

Local loess-like subsoil clays are of considerable interest for the preparation of hydrotechnical cements; these, on being roasted in the range 650-750°, acquire hydraulic properties. Loess cement hardens better in sulfate solutions than in fresh water. The low stability of loess cement to the atmosphere, which is the result of the deleterious action of atmospheric carbon dioxide, may be eliminated by additions of Portland cement. Loess cement of grade "250" has been approved for hydrotechnical construction and is to be recommended as a high-quality hydrotechnical cement. It has been established that synthetic cements consisting of various proportions of calcium monoaluminate and calcium orthosilicate are very resistant to the agressive action of sulfate- and magnesium-containing waters.

Academicians M. M. Dubinin and S. I. Volfkovich and Corr. Memb. USSR Acad. Sci. V. I. Spitsyn took part in the discussion of this paper. They pointed out that hydrotechnical cements were of great importance for the Central Asian Republics, in which one of the greatest works of communism — the construction of the Main Turkman Canal — was being carried out. The utilization of local materials that would improve the quality of the cement was of great practical importance. Hopes were expressed that trials would be made of the effects of additions of surface-active substances at particular stages of the setting and hardening of cement.

Academician S.I. Volfkovich in his paper "Questions of the Chemistry and Technology of Mineral Fertilizers in Central Asia" remarked that the chemization of agriculture presented chemistry, technology, and agrochemistry with immediate problems in the planned study of the optimum conditions for the application of mineral and organic fertilizers under the actual conditions of Central Asia and in the study also of the most suitable means of production, having regard for the raw-material and energy resources and the present-day progress in agrobiology. The speaker cited data on the effectiveness of one ton of nutritive elements in different fertilizers for different types of soils and crops.

The presence of sources of phosphates, sulfur, sulfide ores, potassium and other salts, water power, and fuel in the Central Asian Republics, together with a large demand for fertilizers of high efficiency, makes the problem of the further development here of the manufacture of mineral fertilizers, particularly those providing phosphorous and nitrogen, a very urgent and important one.

It is essential not only to extend the manufacture of superphosphate, but also to study and to bring into use methods of improving the physical properties of superphosphates, increasing the P_2O_5 content, and eliminating the deleterious effect of magnesium compounds on the process. Above all, it is essential to find an effective solution of the difficult problem of enriching phosphorites and to become familiar with processes for the ammoniation of superphosphate and its granulation. By the ammoniation of superphosphate by means of ammoniates it is possible to obtain phosphorous — nitrogen fertilizer containing proportions of nutritive elements close to those required for the main pre-sowing application.

It is possible to obtain another concentrated fertilizer "precipitate" (dicalcium phosphate), containing 32-44% P_2O_5 in a citrate-soluble form. Technically pure dicalcium phosphate is of great interest as a very effective fodder medium for the raising of livestock.

A process that is economical and shows great promise is that for the preparation of "precipitate" with the simultaneous production of calcium or ammonium nitrate by means of a complex process for the decomposition of phosphates with nitric acid. In this process, all the raw material is utilized. In the USSR a number of investigators have developed manufacturing processes for the nitric acid treatment of phosphates not only with the separate preparation of dicalcium phosphate and calcium nitrate, but also with the formation directly of double (nitrogen-phosphorous) or triple (nitrogen-phosphorous-potassium) fertilizers.

Owing to the development of hydroelectic power, the establishment of an electrothermal process for the production of phosphoric acid and its salts (for concentrated fertilizers and feeding media) is of great interest for the future. In the paper, other thermal and thermal-alkaline methods for the treatment of phosphates were discussed. Among nitrogenous fertilizers the most satisfactory appeared to be ammonium nitrate. Calcium cyanamide is not only a nitrogenous fertilizer, but also, it has been shown a defoliant for the cotton plant; it has herbicidal properties. It is possible that the question of its manufacture in the necessary quantities requires further examination. The extension of the manufacture of urea and of its application in agriculture is determined by the economics of production. Potash fertilizers may be suitably applied in Central Asia in the form of concentrated salts: the chloride and sulfate, and in the future, possibly, also the nitrate. It is desirable that part of the fertilizers should be applied as manure mixtures, a suitable component for which is "precipitate" (dicalcium phosphate). The implementation of the directives of the Nineteenth Congress of the Communist Party of the Soviet Union regarding the fertilizer industry in the Fifth Five-Year Plan presents the research organization with great and urgent theoretical and practical problems.

Academician Volfkovich's paper aroused considerable interest in those present at the Session: he had raised a number of questions. The following took part in the discussion of this paper: M. N. Nabiev, Cand. Tech. Sci. Corr. Memb. Acad. Sci. USSR A.F. Kapustinsky, A.D. Petrov, Academician M.M. Dubinin Active Memb. Acad. Sci. UzbekSSR A.S. Sadykov.

The second meeting of the Joint Session under the Chairmanship of Academician V.M. Rodionov and S. Yu. Yunusov, vice-president of the UzbekSSR Academy of Sciences took place on 25th October at the House of Scientists. The first paper of the meeting was given by Active Memb. [illegible] UzbekSSR Academy of Sciences. He discussed the results of investigations of the alkaloid-bearing plants of Central Asia and of their alkaloids; these were carried out in the Alkaloid Chemistry Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences. Since the laboratory was established, about 3000 species of plants have been analyzed, and a number of very valuable alkaloid-bearing species has been found. The contents and also the quantitative and qualitative changes of the alkaloids in different parts of plants have been studies with respect to their dependence on the conditions of growth and the vegetation periods. It has been found that the green part of alkaloid-bearing plants (stalks and leaves) contains the maximum amount of alkaloids before flowering and fruit-bearing; in the underground parts and the bark the amount of alkaloids becomes less during this time.. In dry grass and leaves after the vegetation period there remains a very small amount of alkaloids, and this passes to the underground part and to the seeds, and in the case of woody plants – to the barks.

The reader of the paper and his co-workers have isolated more than 35 new alkaloids: the structures of five of these have been completely proved; for about ten the structures are partially known; and the remainder is being studied.

The following took part in the discussion of this paper: Academicians V.M. Rodionov, M.M. Dubinin, and S.I. Volfkovich, Corr. Memb. Acad. Sci. USSR B.A. Arbuzov, Prof. G. P. Menshikov, and others; they all expressed high appreciation of these investigations and pointed out the correctness of the line of work – the relating of the search for alkaloids with the growth of the plant — and they pointed out the great theoretical and practical significance of these investigations.

Active Memb. Acad. Sci. UzbekSSR A.S. Sadykov gave a paper on results of investigations on the chemistry of the alkaloids of anabasis. In a discussion of work by A.P. Orekhov and G.P. Menshikov in this field, the speaker reported the results of investigations of the transformation products of anabasine and accompanying alkaloids obtained from anabasis, which were carried out in a laboratory under his direction at the Institute of Chemistry of the UzbekSSR Academy of Sciences. The speaker has succeeded in developing a number of methods that enabled anabasine and lupinine to be prepared in appreciable amount and in adequate purity. The oxidation of anabasine and its derivatives and of a mixture of anabasine and lupinine has been carried out with different oxidizing agents, and the course of the oxidation reaction has been elucidated.

The spitting of anabasine at a C-C bond by the aid of aluminum chloride or sodium is an interesting reaction. A detailed study of this reaction with anabasine and other alkaloids (nicotine, salsolidine) enabled a mechanism to be proposed for the process. Sulfonation of anabasine with pyridine — sulfur trioxide in sulfuric acid under various conditions indicated that the secondary nitrogen as a different character in piperidine than in anabasine. Various sulfonation products of anabasine and its derivatives have been obtained and characterized. The reaction of acrylonitrile with anabasine has also been studied. For the cyanoethylation of anabasine, the effect of water on the rate of the reaction has been determined; the results were explained by the speaker by the partial formation of the ammonium base, which is a catalyst. A wide study has been made of the amination of anabasine and its derivatives. Acetyl derivatives of aminoanabasines have been submitted for pharmacological study.

In addition to the study of the chemistry of anabasine, the alkaloids that accompany anabasine are being investigated. Various derivatives of lupinine have been synthesized. Methods have been developed for the isolation of individual alkaloids from a mixture of the bases. A study is being made of the products of splitting afilline and afillidine with sodamide.

The following took part in the discussion of this paper: Academicians V.M. Rodionov and M.M. Dubinin, Corr. Memb. Acad. Sci. USSR N.I. Nikitin, Prof. G.P. Menshikov, and others; they all expressed high appreciation of the investigations on anabasine. Participants in the discussion remarked that the work begun by A.P. Orekhov and G.P. Menshikov had found worthy continuators in the Institute of Chemistry of the UzbekSSR Academy of Sciences. Much that was of interest from the preparative point of view had been done.

In this paper, Academician V.M. Rodionov gave a review of the present state of the investigation of the chemistry of alkaloids and he gave an account of the immediate problems in this field and in the further study of our alkaloid-bearing flora. A review was given of the discovery of plant bases (morphine, quinine, cinchonine, and cocaine) at the beginning of the nineteenth century and of the study of their properties and structures; the significance of these investigations for the development of theoretical and preparative organic chemistry was discussed. The first attempts at an approach to the syntheses of morphine and quinine led to the synthesis of many important compounds. The study of the properties of quinine and of the accompanying alkaloids from cinchona bark were of no less significance for the development of the chemistry of heterocyclic compounds. The subsidiary alkaloids of opium led to the creation of the chemistry of isoquinoline. The first unsuccessful attempts to synthesize quinine led to the discovery of synthetic dyes and the preparation of remarkable medicinals of the pyrazolone series . antipyrine, pyramidone, analgin and others. Investigations in search of substitutes for morphine were very successful and yielded several preparations of pharmaceutical value (demorol, Soviet promedol, which are superior to morphine in sedative properties, and others). Similar results were obtained also in the investigation of cocaine and other alkaloids.

The main significance of alkaloid chemistry consists in the fact that it leads to a deeper study of heterocyclic compounds and to the syntheses of new substances that are valuable in theoretical, biological and practical respects. Much remains in this field, however, that is unsolved or undeveloped. There is no generally accepted view on the functional role of alkaloids in the life of plants, and the significance of the vegetational period for the formation of alkaloids in plants is not fully established. These investigations, which may have also results of practical value, demand much cooperation between organic chemists and biologists (botanists and physiologists).

Insufficient attention has been given to the thorough study of the active principles of alkaloid-bearing plants. In most cases only the alkaloids themselves are studied, to the neglect of the organic acids with which the alkaloids are bound. It is difficult to believe that the acid part is without biological significance. Much more attention must be given to the study of the complexes formed. Apart from these immediate problems, it is very important to elucidate the factors determining the formation of alkaloids in plants and to solve certain other problems closely associated with the physiology of plants. Much work remains to be done also on the further study of our alkaloid-bearing flora.

The paper prompted a large number of questions and other contributions; among those taking part were Academician M.M. Dubinin, Active Members Acad. Sci. UzbekSSR Yu. Yunusov and A.S. Sadykov, Corr. Memb. Acad. Sci. USSR I.N. Nazarov, Corr. Memb. Acad. Sci. UzbekSSR I P. Tsukervanik, Prof. G.P. Menshikov.

The third, and final, meeting of the Joint Scientific Session was held under chairmanship of Corr. Memb. Acad. Sci. USSR B.A. Arbuzov and of Active Memb. Acad. Sci. UzbekSSR A. S. Sadykov on 28th October at the House of Scientists. In opening the final meeting, Academician - Secretary of the Division of Chemical Sciences of the USSR Academy of Sciences M.M. Dubinin gave the sad news of the death of the eminent Soviet Physical chemist Academician Vladimir Aleksandrovich Kistyakovsky. The well known and brilliant investigations of Vladimir Aleksandrovich Kistyakovsky played a great part in their time in the development of Soviet electrochemistry and theory of corrosion. Those present at the meeting paid honor to the memory of V. A. Kistyakovsky by standing.

The first paper was by Corr. Memb. Acad. Sci. UzbekSSR I.P. Tsukervanik on "The Reactions of Acetylene with Aromatic Compounds", in which investigations were described that were based on material relating to the alkylation of the aromatic nucleus with bifunctional compounds.

In reactions with benzene it has been established that addition of $FeCl_3$ and certain other substances to $AlCl_3$ results in an increase in the relative yield of low-boiling fractions, which contain, in this case, styrene (up to 15% of the total yield of products). It has thus been shown that condensation may occur in the direction of the equation $CH \equiv CH + H.Ar \longrightarrow Ar.CH = CH_2$, which is contrary to ideas derived from previous investigations of the impossibility of the formation of aromatic vinyl compounds in this way; ways of creating conditions for the production of higher yields of vinyl compounds can now be indicated.

A detailed study has been made of the condensation of dimethylaniline with acetylene, vinyl chloride, and acetic anhydride in presence of $AlCl_3$ and other catalysts. The conditions have been found for the preparation of di-(p-dimethylaminophenyl)ethane in about 40% yield. The nature of anomalous reaction products has been elucidated: they are leuco bases of di- and tri-phenylmethane dyes.

The previously inaccessible and therefore little studied, 1, 1-diarylethanes are of considerable interest as starting materials for various syntheses: some of them can be utilized directly (as components of lubricating oils, antioxidants, etc.) A study has been made of the chlorination, nitration, and sulfonation of diphenylethane and other substances of this series. The chlorination and nitration products are analogs of well known insecticides of the DDT type; their properties are now being studied in detail.

Academicians V.M. Rodionov and M.M. Dubinin, Active Memb. Acad. Sci. UzbekSSR S. Yu. Yunusov, Corr. Members Acad. Sci. USSR I.N. Nazarov, B.A. Arbuzov, A. D. Petrov, and others joined in the discussion.

Corr. Memb. Acad. Sci. USSR I.N. Nazarov in his paper "The Synthesis of Sedatives" gave a short review of the present state of investigations on the synthesis of sedatives and pointed out that until recently the only preparation having a sedative action was morphine, one of the first organic compounds isolated in a pure form (at the beginning of the nineteenth century) and applied in medicine; he described the work carried out under his supervision on the synthesis of new sedatives.

The problem of synthesizing sedatives is largely equivalent to the development of simple and accessible methods for preparing 4-piperidones. An important step forward in investigations on the synthesis of sedatives was provided by investigations, carried out under the speakers' supervision, on the devising of new simple methods for preparing heterocyclic compounds, particularly 4-piperidones, from acetylene. The principal reactions in these investigations were condensations of ketones with 1-buten-3-yne. The next stage in the synthesis of sedatives is the introduction, in place of the carbonyl radical of the 4-piperidone, of a phenyl radical and an ether group. The final problem in the synthesis of these compounds is the esterification of 4-phenyl-4-piperidinols to give esters of organic acids. Compounds synthesized by the speaker have been thoroughly investigated with respect to their physiological activity under the supervision of Prof. M. D. Mashkovsky.

These syntheses form an important stage in the development of the chemistry of sedatives, for these compounds when their overall properties are considered, are superior to all other such preparations known at present (morphine lydol, phenandol, etc.) They have a comparatively low toxicity combined with a high sedative activity, about three times as great as that of morphine, without having many of the deleterious properties of the latter (habit forming and other accompanying effects), which is a very important advantage. In promedol medicine has an original Soviet preparation having high activity and a wide field of application. Promedol is not the last word in synthetic organic chemistry. In the near future the appearance of new substances having similar properties may be expected.

Academicians V.M. Rodionov and M. M. Dubinin, Active Members Acad. Sci. Uzbek SSR A.S. Sadykov and S. Yu. Yunusov, Corr. Memb. Acad. Sci. USSR B. A. Arbuzov, Corr. Memb. Acad. Sci. UzbekSSR I. P. Tsukervanik, and others took part in the discussion on this paper.

Kh. U. Usmanov, Cand. Chem. Sci., in his paper "Recent Physicochemical Investigations of the Cotton Fiber", gave the results of the first systematic investigations of cotton fibers from a large number of selection varieties, obtained in the Natural Polymer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences and in other institutes of the UzbekSSR Academy of Sciences. On the basis of the results obtained and the results of other investigators of the cotton fiber, the speaker came to the following conclusions:

The fibers of different selection varieties have differing chemical compositions. This difference is found for all the principal substances present in the fiber. The composition depends greatly on the degree of maturity. The degree of polymerization of cellulose varies in different varieties and increases with maturity. This increase is associated with the ripening period of the given variety of cotton plant.

The sorption properties of purified cotton fibers, while varying very little from one variety to another, depend greatly on the degree of maturity. The sorptive capacity of the fiber falls with increasing maturity, the rate of fall being different for different varieties, and being associated also with the ripening periods of these varieties. Sorption and desorption of water by the cotton fiber is slow; this indicates the desirability of constructing cotton driers of the layer type.

The relation between the strength of the fiber and its maturity is different for different varieties. The curve for the dependence of deformation of cotton fibers on their moisture content is of an S-form, and the inflection of the deformation curve for all cellulose fibers corresponds, in general, to the same relative humidity.

The following took part in the discussion of this paper: Academician M. M. Dubinin, Active Memb. Acad. Sci. UzbekSSR A. S. Sadykov and S. Yu. Yunusov, Corr. Members Acad. Sci. USSR N. I. Nikitin and V. A. Kargin, P. I. Zubov, Doc. Sci., V. I. Ivanov, Doc. Sci, Prof. G. D. Vovchenko, Scientific Officers A. S. Sultanov and L. V. Smolina, and others.

The final paper of the third meeting of the Session was given by Corr. Memb. Acad. Sci. USSR V. A. Kargin on the mechanism of the deformation of crystalline polymers.

The speaker pointed out that in the deformation of amorphous polymers all the properties of the material change continuously and the polymer gradually passes from its originally isotropic form into an anisotropic, highly oriented thread. The deformation of crystalline polymers has been regarded in the same way as that of amorphous substances, the difference lying in their content of solid particles—small crystals of the polymer—which play the part of fillers. Investigation of the mechanical properties of such crystalline polymers as polyamides, polyethylene, gutta-percha has shown a great difference in the behavior of this group of polymers. At high deformations the change in properties of these polymers proceeds not continuously, but by a jump — a sudden change of the isotropic material directly into a highly oriented thread.

On the basis of an investigation of changes in polymers at high deformations it has been suggested that the deformation of crystalline polymers occurs by means of a phase transformation of the polymer crystals. Those crystals oriented perpendicularly or at a large angle to the direction of the force are broken down, and at the same time new crystals oriented in the direction of the force are formed.

The hypothesis that high deformations of crystalline polymers occur via phase changes in the crystalline part has been directly proved by an X-ray study of isotropic and stretched films of polyethelene. It was found that conversion of the polyethylene to the oriented state is accompanied by formation of a crystalline modification differing somewhat from the crystals in isotropic polyethylene. The very nature of the change in texture during orientation also indicates the disappearance of those crystals that existed in the original isotropic polymer and the appearance of new crystals oriented in the directions of the stretching forces.

The mechanical properties of crystalline polymers are determined by the peculiarities in structure and properties of the crystalline part, which takes an active part in the deformation processes of the material. The difference in mechanical properties between crystalline and amorphous polymers was shown particularly graphically in the case of natural rubber, which can be obtained in both states at one and the same temperature.

Academician M. M. Dubinin, Active Memb. Acad. Sci. UzbekSSR A. S. Sadykov, Doctors of Science N. V. Mikhailov, V. I. Ivanov, K. G. Trofimov, B. G. Zaprometov, and others took part in the discussion of this paper.

The participants of the Joint Session agreed with great enthusiasm to send a letter of greetings to I. V. Stalin.

Apart from meetings of the Session, a number of conferences were held on particular questions, with detailed examination of the lines of work of Uzbek scientists.

1. Conference on the Chemistry of Mineral Fertilizers

The conference on the chemistry of mineral fertilizers, which took place in the Institute of Chemistry of the UzbekSSR Academy of Sciences under the chairmanship of Academician S. I. Volfkovich, had two plenary and one laboratory sessions, at which the following papers were heard and discussed:

"Physicochemical Analysis of Processes for the Nitric Acid Treatment of Phosphates" by Academician S. I. Volfkovich; "Some Results of the Work of the Fertilizer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences" by M. N. Nabiev, Cand. Tech. Sci.; "Phase Distribution of Fluorine Compounds in the Decomposition of Phosphorite Raw Material with Nitric Acid" by Junior Scientific Worker R. A. Ablyazina; "Nitric-acid Decomposition of Kara-tau Phosphorites, with Precipitation of Calcium by Sodium Sulfate" by F. M. Mirzaev, teacher in the Faculty of Chemical Technology of the Central Asian Pedagogical Institute; "Agrochemical Requirements in Phosphorus and Nitrogen Fertilizers" by B. P. Machigin, Cand. Agric. Sci.

About sixty people took part in the conference; they included Ministry representatives, and workers from fertilizer factories, from a number of institutes of the UzbekSSR Academy of Sciences, from the Samoilov Scientific Institute of Fertilizers, Insecticides, and Fungicides, and from the Cotton Research Institute of the USSR Ministry of Cotton Growing.

Many of those present took an active part in the extensive discussion that the papers provoked; they included not only chemists and technologists, but also biologists, geologists, and agronomists, and it was possible, therefore, to examine thoroughly all aspects of questions concerning the desirable range of fertilizers that should be available and to coordinate several technological questions with the raw-material resources of Central Asia.

The conference noted that the fulfillment of the directives of the Nineteenth Congress of the Communist Party of the Soviet Union (which contemplated an increase of 88% in mineral fertilizers in 1955, as compared with 1950, and the building of fertilizer factories in excess of immediate requirements in order to ensure the necessary development in production in the succeeding years) must proceed by the improvement and intensification of manufacturing processes, improvement of the physicochemical properties of fertilizers, and the search for better methods of incorporating fertilizers in the soil; it must proceed also by the construction of factories for the production of new kinds of fertilizers. These measures are bound to help not only in the production of the additional amounts of mineral fertilizers required, but also in increasing their agrochemical effectiveness.

The main theme of the work of the Fertilizer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences is the solution of problems relating to the improvement of the physicochemical properties of nitrogen and phosphorus fertilizers and to the increase of the resources of these fertilizers by the nitric-acid treatment of phosphorite raw material. The results of experiments by the Cotton Research Institute on the desirability of using the siftings obtained in the production of granulated superphosphate for feeding the soil were noted as being of practical value for the technology of fertilizers.

In order to find out more about the agrochemical value of freshly precipitated tricalcium phosphate, as a product of the nitric-acid treatment of phosphates, it is planned to carry out culture and field experiments with phosphates of this kind, both alone and also in admixture with ammonium nitrate, on the saline soils of Central Asia. It was recognized that work must continue on the desirable ratios of active fertilizer components (P_2O_5 and K_2O) in complex and mixed fertilizers and the way they depend on the period of growth of the cotton plant. It was recommended that work should be intensified in the search for new defoliants for the cotton plant which could be prepared from readily available substances that are less toxic for animals than those used at present. As the application of non-root feeding of plants from planes is of such importance, it is desirable to work on the preparation of dry concentrated fertilizers (ammoniated double superphosphate), and also of the corresponding solutions. It was considered that a discussion was desirable, at a separate conference, of the problems and future prospects of the utilization of Central Asian salt resources.

2. Conference on the Chemistry and Physical Chemistry of Cotton

The conference on the chemistry and physical chemistry of cotton, which took place in the House of Scientists under the chairmanship of Corr. Memb. Acad. Sci. USSR V. A. Kargin, had three sessions, at which the following papers were read and discussed:

"Some Present-day Problems in the Theory of the Structure of Cellulose" by V. I. Ivanov, Doc. Tech. Sci.; "Modern Methods for the Chemical Investigation of the Fine Molecular Structure of Cotton Cellulose" by E. D. Kaverzneva, Doc. Chem. Sci.; "Experimental Data on the Physical Chemistry of the Cotton Fiber at Different Periods of Growth" by Kh. U. Usmanov, Cand. Chem. Sci.; "Dependence of the Technological Properties of the Cotton Fiber on the Maturity of the Boll" by M. K. Aleksandrov, Cand. Tech. Sci.; "Main Results and Future Prospects of Investigations of Selection Varieties of Cotton" by V. V. Laikov, Cand. Tech. Sci.

About seventy scientific workers and specialists in the fields of agrobiochemistry, selection, and the technology of the primary processing of cotton took active part in the work of the conference; they included representatives of the Institute of Chemistry of the UzbekSSR Academy of Sciences, the Institute of Agriculture of the UzbekSSR Academy of Sciences, the Institute of Organic Chemistry of the USSR Academy of Sciences, the Central Research Institute of the Cotton Industry, the Cotton Research Institute, the Central Asian State University, the Institute of Physical Technology of the UzbekSSR Academy of Sciences, the Tashkent Textile Institute, and other scientific institutions and selection stations of Uzbekistan and Tadzhikistan.

In the papers of V. I. Ivanov and E. D. Kaverzneva new data were given concerning the chemical heterogeneity of the molecular structure of cellulose, and it was suggested that these phenomena are connected with processes of formation of cellulose in plants and have a bearing on the chemical treatment of the cotton fiber.

In the papers of Kh. U. Usmanov, M. K. Aleksandrov, and V. V. Laikov, new data were given concerning the changes in the structure and chemical and technological properties of the cotton fiber during the growth of the plant, the most interesting being those relating the length, fineness, strength, and sorptive power of the cotton fiber, and the molecular weight of the cellulose it contains, to the degree of maturity of the cotton.

For a number of these very important technical properties of the cotton fiber an optimum has been established in the course of their changes during ripening, and these relations have not yet been fully explained and taken into account in the theory and practice of selection and cultivation of cotton. Moreover, these relations indicate new ways and possibilities, enabling still greater control over the evolution of the cotton plant with the object of increasing still more the efficiency of its production.

In the discussion on these papers, in which chemists, biochemists, technologists, and selection experts took part, the desire was expressed that further, more concrete, application of the data on the chemical heterogeneity of the cellulose molecule should be made to the problems of the chemistry of cotton in the course of growth, with the object of discovering methods for controlling it. Furthermore, attention was drawn to the fact that the time was now ripe for the scientific institutes of Uzbekistan to tackle new problems on the purification of raw cotton, making use of recent advances in cellulose chmistry, and to continue investigations on the controlled oxidation of the substances accompanying cellulose in the cotton fiber, which might lead in the future to the creation of more rational methods of purifying raw cotton and so to an improvement in the treatment of cotton in the textile industry and to the production of cotton goods of improved quality.

There were detailed discussions of many concrete questions of the theory and practice of cotton production related to the mechanism of the appearance and improvement in the course of ripening of technically important chemical and physicomechanical properties of the fiber. At the same time, attention was devoted to long-term research in this field and also to the methods of conducting team investigations directed to the acquiring of more exact information on the laws relating the properties of cotton to the conditions of growth. Emphasis was laid on the need for the development of rapid chemical and physicochemical methods for following the ripening of the cotton fiber throughout its period of growth.

It was noted that this conference was the first general scientific conference of chemists and specialists in the chemistry and physics of cotton cellulose, and it was emphasized that similar conferences were necessary in the future.

3. Conference on Alkaloid Chemistry

The conference on alkaloid chemistry was held in the small conference hall of the Presidium of the UzbekSSR Academy of Sciences under the chairmanship of Academician V. M. Rodionov. There were three sessions, at which 14 original papers were read on alkaloid chemistry:

"Alkaloids of the 1-Methylpyrrolizidine Series" by G. P. Menshikov, Doc. Chem. Sci.; "Alkaloids of Colchicum" by V. V. Kiselev, Cand. Chem. Sci.; "Investigation of Alkaloid-bearing Plants of Central Asia" by E. E. Korotkova, Cand. Bot. Sci.; "Sulfonation of Anabasine" by O. S. Otroshchenko, assistant in the Department of Plant Chemistry of the Central Asian State University; "Cyanethylation of Anabasine" by E. Kh. Timbekova, undergraduate in the Department of Plant Chemistry of the Central Asian State University; "Investigation of the alkaloids of the following: Haplophyllum (junior scientific worker G. B. Sidyakina); Aconitum and Delphinium

(N. K. Abudakhirova, Cand. Chem. Sci.); Aconitum tellassicum (junior scientific worker G. F. Potemkin); Thalictrum minus (N. N. Progressov, Cand. Chem. Sci.); Vinca erecta (F. Yu. Yuldashev, undergraduate of the Institute of Chemistry); Ungernia Severzowi (Kh. A. Abduazimov, undergraduate of the Institute of Chemistry); Lolium Cuniatum (S. T. Akramov, junior scientific worker); Thermopsis alterniflora (Shch. P. Pakudina, junior scientifc worker); Poisonous Weed of the Borage Family (N. V. Plekhanova, undergraduate of the Institute of Chemistry)"; and "Isomerization of Pseudoephedrine into Ephedrine" by D. M. Guseva, junior scientific worker.

About 70 scientific workers of the institutes of the UzbekSSR Academy of Sciences, the Central Asian State University, and other scientific organizations of Tashkent took part in the work of the conference.

In a series of investigations carried out under the direction of G. P. Menshikov it has been established that the parent substance of all alkaloids of the borage family is the new heterocycle 1-methylpyrrolizidine. A new rational classification of alkaloids of the 1-methylpyrrolizidine series has been proposed. These alkaloids can be divided into four groups: levo-heliotridan, dextro-heliotridan, levo- pseudoheliotridan, and dextro pseudoheliotridan. It has been shown that, when amino alcohols of the 1-methylpyrrolizidine series are oxidized, isomerization occurs with formation of two stereoisomeric acids. The speaker considered that the role and significance of alkaloids in the life of a plant are directly related to the structures of the alkaloids. Alkaloids of differing structures may play quite different parts in the life of the plant.

From a poisonous weed of the borage family, M. V. Plekhanova has isolated two new alkaloids: incanine and incanidine: they belong to the same 1-methylpyrrolizidine series.

From Colchicum (variety Magnificent) V. V. Kiselev has isolated three alkaloids: colchicine, colchamine, and colchicerine. A proof has been given for the structure of the new alkaloid colchamine, at the basis of which lies the same system as that found in colchicine: colchamine differs from colchicine in having methyl instead of acetyl on the nitrogen, and colchamine is therefore decidedly basic in character. It has been established that colchicerine is a molecular compound of colchicine and colchamine.

E. E. Korotkova gave a general exposition of the results of investigations of the flora of Uzbekistan and neighboring republics with respect to their alkaloid-bearing characteristics. Plants have been investigated at various periods of growth, in various vegetative organs, and in various localities. A list, containing about 2300 plants, of the alkaloid-bearing plants of Central Asia has been drawn up and is being prepared for publication. Weeds found in cereal crops have also been investigated for their alkaloid-bearing characteristics.

O. S. Otroshchenko reported on the sulfonation of anabasine with pyridine—sulfur trioxide and sulfuric acid. In the course of this work, 2,3'—bipyridinesulfonic acid, in which the sulfo group is in the α-substituted pyridine nucleus, has been isolated and characterized. At the same time methods have been worked out for the isolation of anabasine from an anabasine—lupinine mixture and the colorimetric determination of anabasine in the general alkaloid mixture.

E. Kh. Timbekova reported on the reactions of anabasine with acrylonitrile in various solvents. N'—Propylanabasine has been prepared and characterized, and it has been subjected to various reactions, as a result of which about twelve preparations have been sythesized and submitted for pharmacological examination. G. B. Sidyakina has isolated two new alkaloids, haploperine and haplophine, from certain varieties of Haplophyllum, and it has been established that both of these alkaloids belong to the quinoline group; a structural formula has been proposed for haplophine. For one of the varieties a study has been made of the total amount of alkaloids and their approximate proportions at various periods of growth. From three varieties of Delphinium, N. K. Abudakhirova has isolated five new alkaloids and has proved the structures, in part, of three of the alkaloids: delsemine, delsemidine, and delphatine. From one variety of Delphinium, two preparations that can be used as substitutes for curare have been obtained. The preparations are undergoing clinical tests and have been accepted by the State Pharmacopeia Council. Work has begun on the determination of the basic skeleton of the aconite alkaloids. From the aerial part of Aconitum tellassicum, G. F. Potemkin has isolated two known alkaloids, talatisine and talatisamine. The structural formula of talatismine has been made more precise. Investigations are being carried out with a view to the determination of the structure of the talatisamine nucleus.

From Thalictrum minus N. N. Progressov has isolated five new alkaloids. It has been established that the alkaloids thalicmine and thalicmidine are aporphine derivatives; the structure of thalicmidine has been proved, and on the basis of a number of regularities to be observed in aporphine alkaloids a structural formula has been proposed for thalicmine. From the aerial part of the plant Vinca erecta F. Yu. Yuldashev has isolated the alkaloid minorine, and from the roots of the plant three new alkaloids, vincanine, vincanidine, and Base No. 3, have been isolated and characterized. It has been established with the aid of dehydrogenation reactions that vincanine contains an indole and pyridine nucleus. A study has been made of the total and relative contents of the alkaloids at different periods of growth.

Kh. A. Abduazimov has investigated tazetine and two new alkaloids, ungerine and ungeridine, isolated from the plant Ungernia Severzowi. Structural formulas have been proposed for the two new alkaloids. It has been established that ungerine belongs to the phenanthridine series. The position of the methylenedioxy group in ungerine has been demonstrated. In an investigation of the poisonous cerial Lolium cuniatum, S. T. Akramov has isolated and characterized the new alkaloid loline. Preliminary results indicate that this alkaloid is a pyrrolidine derivative.

From the seeds of the plant Termopsis alterniflora, Shch. P. Pakudina has isolated five bases: cytisine, pachycarpine, alternine, alternidine, and Alkaloid No. 5. It was shown that alternine and alternidine are condensation products of cytisine and dichloroethane: alternine is an ethylenedicytisine, and alternidine is a chloroethylcytisine. From cytisine a number of preparations have been synthesized and sent for pharmacological examination. The aerial part of the plant has been studied with respect to the variation in alkaloid content with the period of growth. In the early period of growth, the aerial part of the plant could be used as industrial raw material for the preparation of cytisine.

V. M. Guseva has developed a method for the isomerization of pseudoephedrine hydrogen sulfate to give ephedrine in about 90% yield. A search is now being made for a solvent for the separation of ephedrine after the isomerization, when this is carried out under manufacturing conditions.

All the papers gave rise to lively discussion, which yielded much of value to the participants, who had become quite convinced that work on alkaloid chemistry in Uzbekistan is proceeding very vigorously and giving very valuable results. Those taking part in the discussion emphasized the originality of the line of work followed in the laboratory directed by Active Memb. UzbekSSR Acad. Sci. S. Yu. Yunusov, and they pointed, in particular, to the regularities in the dynamics of the accumulation and formation of alkaloids in plants established by workers of this laboratory. Prof. Menshikov's paper was deserving of special attention: the speaker had given an exposition of his work over many years on the pyrrolizidine alkaloids; he had given a new rational classification of these compounds, and had made some valuable remarks on the part played by alkaloids in plants. V. V. Kiselev's paper had made the question of the structures of colchicerine and colchamine perfectly clear.

The twelve papers by coworkers of Active Members UzbekSSR Acad. Sci. S. Yu. Yunusov and A. S. Sadykov gave a vivid picture of the lines of investigation in the UzbekSSR Academy of Sciences. It should be noted that, in a comparatively short period of time, E. E. Korotkova and her team, working in S. Yu. Yunusov's laboratory, have investigated about 70% of all the plants of Uzbekistan.

4. Conference on Organic Synthesis

The conference on organic synthesis took place in the Faculty of Chemistry of the Central Asian State University under the chairmanship of Corr. Memb. Acad. Sci. USSR A. D. Petrov. About eighty persons took part in the conference, and the following papers were read:

"Hydrogenation of Furfural" by A. S. Sultanova and B. A. Maslennikova of the Institute of Chemistry of the UzbekSSR Academy of Sciences; "Petroleum of Lower Uzbekistan" by S. D. Gusinskaya of the Organic Chemistry Department of the Central Asian State University; "Cycloalkylation of Aromatic Compounds" by N. G. Sidorova of the same department; "Radical Alkylation of Aromatic Compounds" by E. A. Vdovtsova of the same department; and "Alkylation with Acrylonitrile" by A. V. Grebenyuk of the same department.

There were lively discussions on these papers, in which a number of critical remarks and practical recommendations were made. The practical importance of investigations of furfural was noted. It was noted also that the investigations of I. P. Tsukervanik's school on alkylation were not only of practical, but also of great theoretical interest, since they threw light on the mechanism of the alkylation process and opened up new ways for the synthesis of biphenyl and bicyclohexane hydrocarbons, which were of interest as model hydrocarbons in the investigation of the kerosene fractions of petroleum.

5. Conference on Coal and Petroleum Chemistry

The conference on coal and petroleum chemistry, which took place in the Institute of Chemistry of the UzbekSSR Academy of Sciences under the chairmanship of Corr. Memb. Acad. Sci. USSR A. D. Petrov, heard papers by the directors of the petroleum and coal laboratories, G. Kh. Kodzhaev, Cand. Chem. Sci., and D. T. Zabramny, Cand. Chem. Sci., relating to the general results of their investigations. Thirty scientific workers of the Institute of Chemistry of the UzbekSSR Academy of Sciences and the Chemistry Department of the Central Asian State University took part in the meeting.

In the discussion of the work of the coal laboratory it was pointed out that serious attention must be given to the important problem of extending resources of coking coals, not only by hydrogenation, but also by other, cheaper methods.

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Apart from the papers given at the main meetings of the Session, and at the specialist conferences, members of the Division, at the invitation of local scientific and public organizations, read a number of papers on questions of interest to scientists and chemists in Tashkent.

On 26 October at the Chemistry Department of the Central Asian State University, a meeting of the Tashkent Section of the D. I. Mendeleev All-Union Chemical Society was held, and papers were read by Corr. Members Acad. Sci. USSR A. D. Petrov and B. A. Arbuzov.

Corr. Memb. Acad. Sci. USSR A. D. Petrov gave a short discussion of the scientific activities of A. M. Butlerov and his students in the Kazan period, and discussed the investigations of Butlerov and his students in the St. Petersburg period in detail. A. D. Petrov devoted special attention to the famous syntheses carried out by the Butlerov school with the aid of organozinc compounds, and he gave a full review of the investigations of A. M. Butlerov's St. Petersburg students and showed in vivid fashion how important these investigations were for the development of organic chemistry.

Corr. Memb. Acad. Sci. USSR B. A. Arbuzov's paper was devoted to a review of the main lines of work of Academician A. E. Arbuzov and his students: a) on the synthesis of organophosphorus compounds; b) on the complex compounds formed by phosphorous esters with certain metal salts; and c) on the application of certain physical methods to the investigation of the structures of organophosphorus compounds.

Corr. Memb. Acad. Sci. USSR A. F. Kapustinsky read a paper at the Central Asian State University entitled "Applications of Physical Chemistry in Geochemistry and Mineralogy" in which he examined, on the basis of a number of examples, the effect of the high pressures existing in the core of the earth on the electron envelopes of the atoms and the conversion of the atoms into the "metallic condition". The basis of the theory of the zonal structure of the earth was explained from the point of view of the theory of atomic structure and thermodynamics, and an exposition was given of the general principles, so important in genetic mineralogy, concerning the sequence of polymorphous changes occurring in crystals as the temperature and pressure rises.

Academician S. I. Volfkovich read a paper in the Polytechnical Institute on the subject of "Crystallization Conditions of Nitrates"; and he read another at the Chirchik Electrochemical Combine on "New Methods for the Manufacture of Nitrogen and Phosphorus Compounds".

Academician A. N. Terenin read a paper in the Central Asian University on "Certain Problems of Photoelectrochemistry".

Prof. G. D. Vovchenko read a paper on "The Palace of our Advanced Soviet Science — the Moscow State University" at the House of Scientists, to a gathering of workers and technologists of the Red Engine Works, and at a meeting of Intelligentsia of Samarkand.

At a well-attended meeting for a wide circle of the intelligentsia of Samarkand, held in the Uzbek State University, Academician M. M. Dubinin discussed the enormous problems facing Soviet chemistry and technology, and Academician A. N. Terenin read a paper on photosynthesis. After these papers, members of the Division answered questions from the audience on matters having a direct or indirect bearing on chemistry.

During their visit to Tashkent, members of the Division of Chemical Sciences gave a number of consultations to workers of the Tashkent chemical institutes.

The participants of the Session visited the tomb of Honorary Academician I. A. Kablukov, who died at Tashkent in 1942.

The participants of the Session visited the Stalin Millionaire collective cotton farm and a number of industrial undertakings.

CONCLUSION

The Session was a successful and lively one. All members of the Visiting Session of the Division of Chemical Sciences took an active part in its work. Attention should be drawn to the business-like character of the proceedings and to the interest taken in the work of the Session by scientific workers of Tashkent and other cities of Uzbekistan, and by workers from neighboring republics. The general Session and the specialist conferences went smoothly and had valuable results. A great part of the time was spent in discussion of the papers, and this formed a most valuable part of the work of the meetings. The attendance at the meetings was always high: at the first meeting of the Session more than four hundred were present.

Particular mention must be made of the meeting at Samarkand, in which a wide circle of the intelligentsia of the city took part: more than seven hundred were present.

Moscow and Leningrad chemists made the acquaintance of Uzbekistan chemists and visited the chemical laboratories of the scientific institutes of Tashkent and Samarkand. Scientific contact was effected not only at the meetings of the Session and at the conferences, but also in personal conversations and consultations, etc., which were of great value. This Session has been a great step forward in the establishment of still closer contact between the young chemistry of Uzbekistan and the central research institutes of the USSR Academy of Sciences.

The resolutions passed at the specialist conferences, together with the discussions of the papers read at the meetings of the Session, have created conditions for the attainment of new successes in the development of chemistry in Uzbekistan, and they are contributing to the rise in the creative activity of scientists that is required for the performance of the tasks, stated in the resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union, which are associated with the new powerful uplift that is taking place in the national economy of the country. It must be considered that the main tasks of the Joint Session have been successfully carried out.

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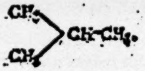
GEOMETRIC ISOMERISM AND PROPERTIES OF COMPLEX COMPOUNDS

I. I. Chernyaev

From the point of view of a chemist investigating complex compounds and therefore accustomed to working with the concept of the central atom, the difference in properties between ordinary structural isomers follows quite naturally from general chemical ideas concerning the undoubted and necessary dependence of the properties of a substance on its structure. If we take any example of isomerism, say butane-isobutane, then actually, no carbon atom can be found in one isomer that has an inner sphere identical in composition with the inner sphere of a carbon atom of the other.

Let us examine, as an example, the second carbon atom in the butane molecule $CH_3-CH_2-CH_2-CH_3$ and compare the composition of its inner sphere with that of the inner sphere of the second carbon atom in the isobutane molecule



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH-CH_3.$$

It will be seen that in butane the inner sphere is composed of methyl, methylene, and two hydrogen atoms, whereas in isobutane there are three methyls and a hydrogen. Hence, in this case it is quite immaterial what we take as our basis in explaining the difference in the chemical reactions of the isomers: the central atom concept, or the concept of the differentiation of the molecules, each considered as a whole. A distinction in chemical properties is obtained, independently of the way in which we regard the structure of the molecules. Thus, the difference in the chemical behavior of the two isomers is not at all surprising, but appears, on the contrary, to be less than would be expected, for in the whole butane molecule it is impossible to find a carbon atom having an inner sphere of identical composition with that of any of the carbon atoms of the isobutane molecule. This equivalence between the approach from the point of view of the composition of the inner sphere of a central atom and the usual method of organic chemists—the determination of the degree of chain-branching and of the distribution of bonds—is altogether to be expected, for the theory of the structure of complex compounds is in essence a development of the same Butlerov theory of structure. However, with the assumption that the differing behavior of isomers depends only on the composition of the inner sphere, the possibility of explaining this difference in behavior on the basis of the mutual effects of atoms composing the molecule moves into the background, for it may be found that this difference in the composition of the inner sphere is quite sufficient to explain the differing behavior of isomers.

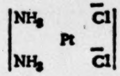
If we take an analogous example from complex compounds, then it is quite obvious that the following isomers

$$[(NH_3)_3ClPt]\,[PtNH_3Cl_3] \text{ and } [Pt(NH_3)_4]\,[PtCl_4]$$

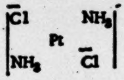
will differ greatly in their chemical behavior, quite independently of the presence or absence of any mutual effects between atoms entering into the inner sphere of the complex. Sufficient cause for their differing behavior is to be found in the fact that the first salt dissociates into singly charged ions, whereas the second gives two doubly charged ions—a difference that is of the same order as that between two carbon compounds containing a double and single bond respectively. On the other hand, the difference in properties may nevertheless depend, in the isomers that we have examined, on the differing spatial arrangement of atoms in the molecule, which in the organic isomers leads to a different degree of chain-branching, and in the complex compounds to a differing spatial arrangement of bonds with the central platinum atom.

To define the extent to which the difference in properties in these isomers is to be attributed to differences in build-up and the extent to which it is to be attributed to differences in spatial arrangement is at present quite impossible, and the only approach to this problem is a study of the difference in properties of geometric isomers. In this particular case of isomerism the whole of the difference in properties must arise from purely spatial causes. However, for many properties this difference is not very great, which, at a first glance, suggests comparison with optically active enantiomorphs, which differ from one another only in the sign of rotation. The cause of the absence of a distinction in properties between stereoisomers is clear: no work is expended in the process of converting one stereoisomer into the other, and the energies of the stereoisomers are therefore identical.

It has been found that the difference in energy between the geometrically isomeric diammines of bivalent platinum — the simplest example of geometric isomerism and the one that was first discovered — is about 3 kcal per mole (V. A. Palkin's determinations). This energy may be regarded as the heat of conversion of one isomer into the other, and the sign of the heat of conversion is in accord with the requirements of electrostatics: 3 kcal is evolved in the conversion of the cis-diammine into the trans-diammine.



$$\left|\begin{array}{ccc} NH_3 & & \overline{Cl} \\ & Pt & \\ NH_3 & & \overline{Cl} \end{array}\right|$$



$$\left|\begin{array}{ccc} \overline{Cl} & & NH_3 \\ & Pt & \\ NH_3 & & \overline{Cl} \end{array}\right|$$

As will be seen from the diagram, this change is accompanied by a separation of the negative charges from one another, which naturally leads to evolution of heat. The thermal curves of the cis and trans isomers give further confirmation of the greater thermal stability of the trans isomer: its decomposition begins 50° higher than that of the cis isomer. In the case of cobalt compounds the isomers are appreciably different in color; the platinum isomers do not differ so much: the trans compound is generally somewhat lighter in color. The ultraviolet absorption spectra of solutions show a difference marked not so much by a change in character as by a regular displacement of the absorption curves (A. V. Babaeva).

There is an appreciable difference in the dipole moments which is always in accord with the accepted structure, the cis isomers having higher dipole moments than trans isomers. There is a difference, not very great, also in dielectric constant. The difference in refractive index is again not very great, but it may be used for determining the configuration. The crystal structure, as determined by the aid of X-rays, while confirming the different disposition of inner-sphere substituents in geometric isomers, does not reveal any particular difference in their distances from the central atom. The melting points are different, but the differences are not very great — not hundreds of degrees, but ten or so at the most. There are appreciable differences in solubility (the trans compound is generally not as soluble as the cis), for in the process of dissolving a chemical reaction occurs and the differences between geometric isomers become quite notable in chemical reactions. Geometric isomers of platinum possess, in fact, a property that permits them to be readily distinguished from one another: the differing speeds of the chemical reaction of displacement in the inner sphere and the resulting difference in type of chemical reaction.

We will cite some examples. As Kurnakov showed, sixty years ago, thiourea reacts with cis-dichlorodiammines, giving tetrathiourea derivatives according to the equation:

$$(NH_3Cl)_2Pt + 4Thio \rightarrow (Thio)_4PtCl_2 + 2NH_3,$$

and with trans-dichlorodiammines, giving mixed trans derivatives according to the equation:

$$(NH_3)_2Cl_2Pt + 2Thio \rightarrow (NH_3)_2(Thio)_2PtCl_2.$$

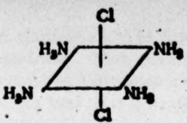
In the first case ammonia is displaced by the urea, and in the second case this does not occur (thiosulfates and sulfites react with diammines in a similar way). Nitrodiammines show the same difference when reacting with amines. Thus, when the cis-dinitrodiammine reacts with pyridine, ammonia is displaced according to the equation:

$$(NH_3NO_2)_2Pt + 2Py \rightarrow (PyNO_2)_2Pt + 2NH_3.$$

The trans-diammine, as will be seen from the equation:

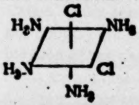
$$(NH_3)_2(NO_2)_2Pt + Py \rightarrow (NH_3)_2PyNO_2PtNO_2,$$

unites with pyridine, giving a triammine. In this case, again, the reactions lead to compounds of completely different types. It is remarkable that the same sort of thing occurs also with quadrivalent platinum — and not only in replacement reactions, but also in reductions to the bivalent state. Thus, trans-dichlorotetrammines are reduced according to the equation:



$Cl_2 + 2H \longrightarrow (NH_3)_4PtCl_2 + 2HCl$

and cis-dichlorotetrammines according to the equation:



$Cl_2 + 2H \longrightarrow (NH_3)_3ClPtCl + HCl + NH_4Cl$

As will be seen from these equations, in the first case bivalent platinum tetrammines are formed, and in the second case triammines. We again observe different types of reactions depending on the geometric structure of the inner sphere. We will cite one further example of the difference in the reactions of isomers. This example was discovered much earlier than the preceding ones by Jörgensen, who found, when studying the effect of hydrochloric acid on isomeric tetrammines, that cis-tetrammines give only one product in this reaction —a mixed trans-diammine according to the equation:

$$(NH_3Py)_2PtCl_2 + 2HCl \rightarrow NH_4Cl + PyHCl + NH_3PyCl_2Pt;$$

whereas trans-tetrammines give two compounds differing in composition, according to the equations:

$$(NH_3)_2(Py)_2PtCl_2 + 2HCl \rightarrow 2NH_4Cl + Py_2Cl_2Pt; \quad (1)$$
$$(NH_3)_2Py_2PtCl_2 + 2HCl \rightarrow 2PyHCl + (NH_3)_2Cl_2Pt. \quad (2)$$

The examples that I have quoted are not isolated ones, but are typical for whole classes of compounds having identical geometrical structure, but different build-up, and are therefore, characteristic not of the molecule or ion entering into reaction, but of the inner sphere of the reacting complex compound. This means that a knowledge of this difference may enable a more precise picture of the chemical structure of the inner sphere to be obtained. Also, the difference in the reactions is not confined to their results, but it is found that the reaction process itself often shows a difference that is not less than the difference in the composition of the product. It is remarkable that this considerable difference in the chemical behavior of isomers was originally interpreted as a consequence of their differences in chemical structure, which was then assumed to be exactly like that of carbon compounds.

As soon as Werner's coordination theory was established, there arose a tendency to supplement the description in terms of this theory of the properties of geometric isomers by reactivity factors, using, in one way or another, the methods developed from structural theory as applied in organic chemistry. The reason for this tendency was the conviction that such fundamental differences in chemical behavior could not be explained in terms of only spatial differences in the disposition of atoms in geometric isomers.

It would be on the whole superfluous to give an exposition of the attempts that have been made to apply structural concepts that are completely incompatible with the possibility of geometric isomerism, but the ideas of Kurnakov, which are of interest in this respect, may be cited. Kurnakov considered that geometric isomerism is possibly associated with the structural method by which the bond halogen—nitrogen (which coexists with the bond halogen —metal) is formed. Schematically, the state of halogen in cis compounds will be represented from this point of view as N—Cl—Pt, and in trans compounds as $\mathrm{N{-}\overset{\overset{N}{|}}{Cl}{-}Pt}$. Kurnakov came to this conclusion on the basis of investigations of the physical properties of complex compounds. However, chemical properties, which indicate a weakening of bonds in trans compounds, are in conflict with this suggestion: for formation of bonds with two nitrogens in trans compounds is bound to strengthen the platinum-chlorine bond. Also, the possibility of indicating the increase in mobility of halogens placed trans to one another by a change in the structural formulas, or, more accurately, by a special disposition of valency units, is rather remote. This will be clear from the following considerations: with continuous change in temperature or solvent properties, the mobility of the halogens will also change continuously, though it is obvious that it is quite impossible to make these changes continuously by means of any change in the separate valency units.

If Kurnakov's point of view were correct, then the difference in properties between geometric isomers would depend not only on the spatial arrangement of the constituent atoms, but also on the difference in the compositions of the inner spheres of the atoms united to the central atom. It is clear that for the chlorines found in cis and in trans positions, the compositions of the inner spheres are quite different: in one case two nitrogens and platinum are to be found in the inner sphere, and in the other case one nitrogen, a chlorine, and a platinum are to be found. Thus, there is a difference even in type of compound. Hence, the possibility of the direct action of inner-sphere substituents on one another must be excluded, for this direct action finds expression as the presence of a valency bond, if it is translated into the language of the theory of structure.

However, the limitation of the number of valency units remains true for the chemistry of complex compounds. Hence, if the correctness of the theory of structure is accepted, then the question of the mutual influence of atoms not directly united to one another must be discussed in terms other than valency units, which are fitted for the expression of the changes of atoms that are directly united together. If, therefore, we wish to express in some way or other the mutual influence of two chlorines in ammonium chloroplatinate or of two hydrogens in hydrocarbons, then for the representation of this process we must always introduce the central atom as a transmitter of this influence. In other words, if it is necessary to express (formally) in some way the interaction of two atoms, then the results of an examination of a three-body problem must be brought to bear on the question. That is to say, the problem of expressing mutual influence in the simplest possible case is as much more complex than the problem of a bond as the three-body problem is more complex than the two-body problem. Consequently, there is nothing surprising and nothing that is contrary to the principles of the theory of structure in the fact that the mutual influence is effected through the central atom.

This mutual influence, when it is assumed to be transmitted only in the trans direction, is fully sufficient to explain the difference, of which I have given examples above, in the chemical behavior of geometric isomers. In addition to its direction, this mutual influence must be ascribed also a definite sense, revealed as a weakening of the trans bond or, what amounts to the same, an increase in the mobility of the trans substituent, whatever its chemical character may be. This "trans effect" does not preclude the possibility of a cis effect, but only under one condition, namely that the "cis effect" also, which naturally has the opposite sign to that of the trans effect (i.e., reduces the mobility of the inner-sphere substituents), shall be effected through the central atom. I shall not cite further examples of the manifestation of the trans effect in the substitution reactions of complex platinum compounds: In a recent article I published a collection of such examples in connection with a discussion on the trans-effect principle. Also, I shall not consider cases of reactions with complex compounds that are not entirely explicable from the point of view of the trans effect· these also were enumerated in the same article; they are few, and they have not yet been fully investigated. In any case, the trans effect can form the basis of further investigations in the chemistry of complex compounds, and for this reason the theoretical basis of this phenomenon and the determination of the extent to which it may be applied to elements other than platinum are of considerable interest.

It is most probable that it results from certain very general properties of the atom that are not yet amenable to precise investigation. The attempt to express the trans effect as a consequence of resonance structures, as Syrkin did, must be rejected. Syrkin was unable to extend his "explanation" to quadrivalent platinum and other elements having an octahedral configuration. For this same reason the American reviewers Quagliano and Schubert also confined their treatment to bivalent platinum, i.e., did not give a full treatment of the subject. Nevertheless, in the chemistry of quadrivalent platinum and cobalt the trans effect is manifested no less clearly than in that of bivalent platinum, i.e., the octahedral configuration is in this respect in no way different in principle from the square configuration; conclusions drawn from the trans-effect principle for quadrivalent platinum are, as a rule, borne out in practice.

One of the problems in the investigation of complex compounds is the provision experimentally of examples of geometric isomerism for as many as possible of the elements that give complex compounds. It is probable that the absence, in the case of many of the elements, of the geometric isomers predicted by theory, results simply from insufficient study of the chemistry of these elements and from the primitive methods of synthesis so far applied in inorganic chemistry. Another general problem relating to the trans effect is to find an approach to the explanation of the small difference in physical properties between isomers when considered in relation to the enormous difference in their chemical behavior, a fact that is in conflict with normal electrostatic concepts. We have the paradoxical position, that the cause of the increased reaction rate in the trans position is a more powerful factor than the electric field in the molecule, but that the trans effect, as it is manifest in a nonreacting molecule, has, for some reason or other, an extremely feeble effect on the physical properties of the molecule. Even the fact that the trans effect of the molecule in the solid is insignificantly small is of fundamental importance, for, as it is absent, we may regard the trans effect as something that arises in the very moment of reaction in the inner sphere and is nonexistant in the resting molecule.

Investigations carried out under the influence of the idea of the trans effect have been based on the assumption that this phenomenon is elementary in character, i.e., it has been assumed that, for example, the order of substituents according to the magnitudes of their trans effects is independent of the nature of the central atom, is independent also of the chemical function of the substituent that is entering the inner sphere, and is still less dependent of the cis addend. Actually, however, no one has really analyzed the position in order to discover to what extent the circumstances that I have enumerated give evidence of the elementary nature of the inner-sphere reactions in which the trans effect is manifest.

A systematic investigation should be undertaken of the behavior of complex compounds formed by various central atoms in various solvents, in order to elucidate the effect of the medium on the trans effect. It is known that the chemical nature of the solvent can change reaction rate by a very high factor (Menshutkin). The question arises, whether this change in rate, which will probably occur also for complex compounds, will be different for cis and trans substitutions. Is it possible for a transition from trans laws to cis laws, or the formation of a mixture of geometric isomers, to take place only by changing the solvent? It has, in fact, been shown by experiment, that the formation of a definite geometric isomer does not depend on the trans effect of the group entering the inner sphere, but only on the substituents already attached to the central atom. When this fact is taken into account, it is difficult to suppose that the solvent will play a determining role in geometric isomerism, but experiments in this direction are nevertheless very desirable.

There is a very real need for the discovery of unequivocal methods of determining the state of atoms in the molecule of a complex compound and for the determination of the nature of the bonds in the molecule. In the present state of the question it is in general impossible to design any experiments (having a chance of being successful) based on the concept of a definite type of bond, and at the same time the question of the selective character of the bonds in a complex compound is in need of solution. I have in view the discovery of some method, even an approximate one, of determining the strength of the bonds of the central atom with any substituent, the strength of the bond formed by this atom with oxygen, for example, being taken as a starting point. It is of interest that the trans effect gives a certain indication of the changes in the strengths of the bonds, but it is not a simple problem to derive absolute values of bond strengths from the trans effect. It is very possible that a solution of this problem may be approached by the discovery of a quantitative characterization of the trans effect expressed in arbitrary units.

In the present Five Year Plan, a fairly wide scheme of investigation is contemplated having as its aim the initiation of work on the quantitative determination of the magnitude of the trans effect. Apart from the obtaining of data on rates of substitution in the inner sphere, other methods of measuring the trans effect will be developed, mainly by the determination of the physical properties of geometric isomers. One of the most important methods suitable for exact measurement is that depending on the investigation of the crystal structures of complex compounds. It is probable that exact determinations of interatomic distances will enable the way in which the trans effect depends on interatomic distances to be found, although it is not altogether certain that such dependence exists. One of the most interesting directions for investigation lies in the determination of the effect of geometric isomerism on the arrangement of atoms in the crystal, for even a partial solution of this problem enables an approach to be made to the determination of the nature of the forces participating in the formation of structures consisting of molecules, not ions, and if a complete solution is found it will be possible to predict the crystal structures of all geometric isomers on the basis of a determination of the structure of one of them.

If the search for a quantitative characterization of the trans effect leads only to a perfection of methods of determining heats of reaction and of electrical and optical properties of complex molecules, to the discovery of some quantitative relations between changes in these properties and the structures of the compounds, and to nothing more than these, even then the trans effect will have acted as a stimulus to the further development of science. However, the further we go, the greater are the number of questions that arise in connection with the trans effect, and it seems to me that the problem of the trans effect will be solved completely only in the very distant future. In the near future, apart from the determination of the physical properties that I have enumerated, it is necessary to intensify work on the synthesis of complex compounds with a view to the investigation of new types of isomerism. The possibilities of synthesizing complex compounds of new types are still far from exhausted, and it must always be remembered that every synthesis of a new compound and proof of its structure constitutes not only the establishment of the fact of the existence of this compound, but, at the same time is a service to the further development of science.

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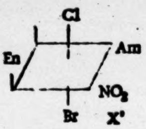
GEOMETRIC AND ENANTIOMORPHIC ISOMERISM OF THE TRIAMMINES $[EnAmPtClBrNO_2]X$

I

In previous work [1, 2] we have studied the geometric isomerism of a new type of cyclic triammine having three different acid groups in the inner sphere, the example taken being the compound $[EnNH_3PtClBrNO_2]Cl$. By making use of the trans-effect principle, we succeeded in preparing the first five of the six possible isomers of this compound. They were all found to be quite stable compounds, differing in chemical and physical properties.



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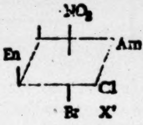

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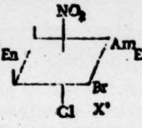

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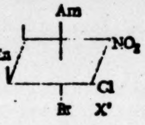

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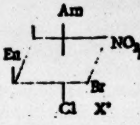

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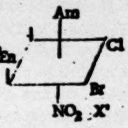
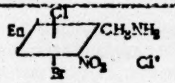
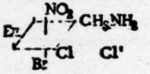


(VI)

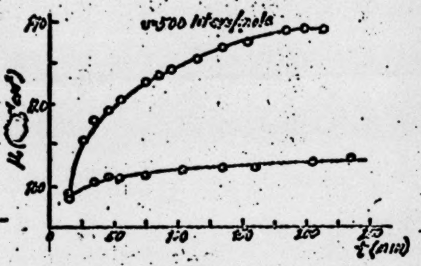
TABLE 1

Properties	 Isomer I	 Isomer II
Color	Pure yellow	Lemon yellow
Solubility at 25° (%)	45.14	27.30
Refractive indices	Ng = 1.75–1.76 Np = 1.714	$N_1 > 1.78$ $N_2 = 1.76$
Action of alkalis	Forms soluble products (of hydrolysis ?)	Forms the crystalline amido compound $EnCH_3NHClNO_2BrPt$
Action of ammonia	Forms the cis-tetrammine $EnCH_3NH_2NO_2NH_3BrPtCl_2$	Reversible interaction
Action of nitrites	Forms the cis-dinitrotriammine $EnCH_3NH_2NO_2 \cdot NO_2BrPtCl$	Reversible interaction

We decided to prove that for this type of compound, as for the previously studied dichloronitrotriammines $[EnAmPtCl_2NO_2]Cl$ (where Am = NH_3, CH_3NH_2, $C_2H_5NH_2$) [3, 4, 5], change in the composition of the ammine part of the molecule should not effect the direction of inner-sphere replacement reactions. For this purpose we investigated the geometric isomerism of the methylamine triammine $[EnCH_3NH_2PtClBrNO_2]Cl$. In the present communication we publish data on the synthesis of the first two isomers, and these fully confirm the correctness of the supposition we have expressed. Both compounds were prepared by procedures similar to those used in the synthesis of the ammonia compounds. Investigations of their properties showed that replacement of ammonia by methylamine has no appreciable effect on chemical properties. A comparison of the properties of the isomers is made in Table 1 and in the Figure.

While studying the geometric isomerism of the ammonia and methylamine triammines $[EnAmPtClBrNO_2]Cl$, we also attempted a comparative investigation of their optical activity. An interesting peculiarity of this type of compound is that all six possible geometric isomers should also possess enantiomorphs. In a number of investigations, begun by Chernyaev and continued by him in conjunction with Litvak, of the triammines $[EnAmPtCl_2NO_2]Cl$, where Am = NH_3, CH_3NH_2, Py [6, 7], and $[EnAmPtCl_2(NO_2)_2]$ [4, 7], it was shown that geometric isomerism and the composition of the ammine part of the molecule have appreciable effects on the sign of rotation and on the coefficient of amido-inversion. Change in the composition of the acid substituents also has an appreciable effect on the rotation coefficients. It was of interest to observe the effect of the introduction of bromine on the optical activity constants of the compound.

Unfortunately, all attempts to separate either the ammonia or the methylamine triammines of structure I



Molecular conductivity of isomeric triammines:
—— Isomer I
—— Isomer II

into their enantiomorphs in the form of hydrogen d-tartrates, d-camphorsulfonates, and α-bromo-d-camphorsulfonates did not give positive results. The solubilities of the diastereoisomeric forms are evidently very close together. The corresponding triammines of the dichloronitro series $EnAmNO_2Cl_2PtCl$ do not possess enantiomorphs.

We succeeded in separating isomers of structure II, $EnNH_3ClNO_2BrPtCl$ and $EnCH_3NH_2ClNO_2BrPtCl$ into their enantiomorphs in the form of hydrogen d-tartrates. The results of our determinations of specific and molecular rotation, dispersion coefficient, and amido-inversion coefficient for these compounds are given in Table 2, and for comparison data for the corresponding dichloronitrotriammines are given also. Dispersion coefficients α_F/α_C had to be replaced by the ratio α_E/α_C in all cases, because the salts under investigation were colored and measurement of α_F for them was rendered very difficult on account of absorption.

The feature that is immediately evident on comparing our results is the identical sign (++) of the difficultly soluble combinations $EnNH_3ClNO_2BrPtC_4H_5O_6$ and $EnCH_3NH_2ClNO_2BrPtC_4H_5O_6$. In the case of the dichloronitrotriammines $EnNH_3Cl_2NO_2PtCl$ and $EnCH_3NH_2Cl_2NO_2PtCl$, on the other hand, replacement of ammonia by methylamine leads to change in the sign of rotation, although the solubilities of the hydrogen tartrates of the dextro and levo enantiomorphs are considerably closer for the methylamine triammine than for the ammonia triammine [1, 3]. It is evident that when bromine is introduced the relation between the solubilities of the diastereoisomeric forms changes further, proceeding as far as a change in sign of the difficultly soluble combination. It would be interesting to verify whether the same picture is to be observed when these compounds are crystallized out as salts of other active acids.

The introduction of bromine results in a considerable approach in the amido-inversion coefficients of the two triammines (they are practically equal: $\rho \sim 5-6$), whereas for the dichloronitrotriammines this coefficient increases 5–7 times on going from the ammonia to the methylamine compound ($\rho_1 \sim 4$; $\rho_2 \sim 21-29$).

The rotatory power of the methylamine triammines is less than that of the ammonia triammines. In the case of the ammonia triammines, replacement of one chlorine by bromine results in a notable reduction in the rotation ($[M]_{D_1} = 40°$; $[M]_{D_2} = 14°$). The coefficient ρ rises somewhat at the same time. The dispersion also increases, owing to the brighter color of $EnNH_3ClNO_2BrPtCl$ in comparison with $EnNH_3ClNO_2ClPtCl$.

In the case of the methylamine triamines it is impossible to form an opinion concerning the relation between the rotatory powers, for $EnCH_3NH_2ClNO_2ClPtCl$ was not cleanly separated into its enantiomorphs and it was not found possible to isolate the second (levo) enantiomorph of $EnCH_3NH_2ClNO_2BrPtCl$. Nevertheless, the agreement between results for the dextro enantiomorphs obtained in parallel experiments ($[M]_{D_4} = 8.68-9.05$) gives reason to believe that it was isolated in an adequately pure form. The lowering of the dispersion coefficient for the dextro enantiomorph in comparison with that of the ammonia compound may be explained by the fact that the measurements were carried out on the nitrate, which is somewhat lighter in color than the chloride.

Thus, the introduction of bromine into the dichloronitrotriammine molecule has an appreciable effect on the rotatory power and on the relation between the ρ coefficients and the signs of the more difficultly soluble combinations for the ammonia and methylamine triammines.

EXPERIMENTAL

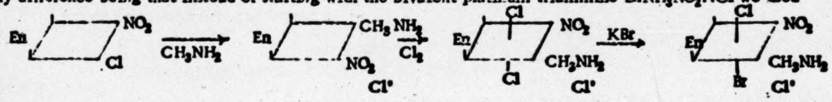
I. Synthesis of $EnCH_3NH_2NO_2ClBrPtCl$ (Isomer I)

We synthesized isomer I following the method used for the corresponding ammonia compound [1], the

TABLE 2

Compound		Sign of the difficultly soluble combination	$[\alpha]_D$	$[M]_D$	α_E/α_C	ρ
1. $EnNH_3ClNO_2ClPtC_4H_5O_6$	[6]	(++)				
$\underline{d}$-$EnNH_3ClNO_2ClPtCl$			+ 9.55	+ 40.54	+ 1.79	+ 4.23
$\underline{l}$-$EnNH_3ClNO_2ClPtCl$			− 2.5	− 10.0	2.00	3.68
2. $EnCH_3NH_2ClNO_2ClPtC_4H_5O_6$	[4]	(−+)				
$\underline{l}$-$EnCH_3NH_2ClNO_2ClPtCl$			− 1.86	− 8.16	2.14	29.5
$\underline{d}$-$EnCH_3NH_2ClNO_2ClPtCl$			+ 0.67	+ 3.06	2.16	20.79
3. $EnNH_3ClNO_2BrPtC_4H_5O_6$		(++)				
$\underline{d}$-$EnNH_3ClNO_2BrPtCl$			3.02	14.16	2.10	5.83
$\underline{l}$-$EnNH_3ClNO_2BrPtCl$			− 2.81	−13.18	2.22	5.92
4. $EnCH_3NH_2ClNO_2BrPtC_4H_5O_6$		(++)				
$\underline{d}$-$EnCH_3NH_2ClNO_2BrPtNO_3$			1.70	8.68	1.50	5.09
			1.78	9.05	1.30	4.99

only difference being that instead of starting with the bivalent platinum triammine $EnNH_3NO_2PtCl$ we used



the corresponding methylamine compound. The intermediates required were prepared by the method previously described [4].

The labile place in the molecule $EnCH_3NH_2NO_2Cl_2PtCl$ is the coordinate Cl−Cl. One of the chlorines of this compound may be readily replaced by ammonia with formation of the cis-tetrammine $EnCH_3NH_2NO_2NH_3ClPtCl_2$, and by the NO_2 group with formation of the cis-dinitro compound $EnCH_3NH_2NO_2NO_2ClPtCl$; in a similar way by the action of the theoretical amount of potassium bromide, one atom of chlorine is replaced by bromine with the formation of a compound corresponding in composition and structure to isomer I. The reaction proceeds when the reaction mixture is heated on a water bath for one-two hours and then evaporated until crystallization begins. The compound is a pure-yellow substance and crystallizes without water.

Found %: Pt 40.63; 40.62; 40.23; Br 16.55; Cl 15.86.
$EnCH_3NH_2NO_2ClBrPtCl$. Calculated %: Pt 40.40; Br 16.56; Cl 14.67.

In full accord with the configuration of isomer I, the compound that we prepared readily reacts with replacement of the chlorine, which is labilized by the trans-active bromine. By the action of ammonia in theoretical quantity or in excess, the cis-tetrammine $EnCH_3NH_2NO_2NH_3BrPtCl_2$ was obtained. Only chlorine occurs in the inner sphere of this compound, a fact shown by potentiometric titration of the outer-sphere halogen. Consequently, the bromine is in the inner sphere and the original triammine is indeed compound I and not its isomerization isomer $EnCH_3NH_2NO_2Cl_2PtBr$.

Found %: Pt 39.51; Br 15.12; Cl 15.21; Cl_{ion} 13.92.
$EnCH_3NH_2NO_3NH_3BrPtCl_2$. Calculated %: Pt 39.02; Br 15.97; Cl_{ion} 14.17.

The inner-sphere chlorine is readily replaced also by a nitro group. When a cold, slightly alkaline concentrated solution of $EnCH_3NH_2NO_2ClBrPtCl$ is treated with sodium nitrite, the reaction mixture becomes appreciably lighter in color and after a time a lemon-yellow substance begins to separate; it corresponds in composition to a cis-dinitro compound.

Found %: Pt 39.27; 39.55; 39.36; Br 16.07; Cl 7.73
$EnCH_3NH_2NO_2NO_2BrPtCl$. Calculated %: Pt 39.54; Br 16.18; Cl 7.17

It is possible, without isolating the chloride, to isolate the amido compound $EnCH_3NHNO_2NO_2BrPt$, by treating the reaction mixture with excess of alkali. The amido compound is a bright-orange substance that crystallizes well.

Found %: Pt 42.96; 42.85
$EnCH_3NHNO_2NO_2BrPt$. Calculated %: Pt 42.69.

In the same way as compounds of similar structure, the dichloronitrotriammines $EnAmNO_2Cl_2PtCl$ ($Am = NH_3$ and CH_3NH_2) and the ammonia bromochloronitrotriammine $EnNH_3NO_2ClBrPtCl$, the compound that we have prepared does not give an amido compound on treatment with alkalis: its solution in caustic alkali takes up a bright color that gradually grows darker.

It was shown for the ammonia triammine $EnNH_3NO_2ClBrPtCl$, that the formation by the action of potassium bromide on $EnNH_3NO_2Cl_2PtCl$ of this bromochloro compound instead of a mixture of dichloro and dibromo derivatives is to be attributed to the double-decomposition reaction that occurs between these compounds:

$$EnNH_3NO_2Cl_2PtCl + EnNH_3NO_2Br_2PtCl \rightarrow 2EnNH_3NO_2ClBrPtCl.$$

This is equally true also for the methylamine triammine $EnCH_3NH_2NO_2ClBrPtCl$.

The trans-dibromo derivative $EnCH_3NH_2NO_2Br_2PtCl$ was prepared by the oxidation of $EnCH_3NH_2NO_2PtCl$ by bromine.

Found %: Pt 36.52; 36.68; Br 31.02; Cl 6.40.
$EnCH_3NH_2NO_2Br_2PtCl$. Calculated %: Pt 36.99; Br 30.28; Cl 6.71

When an equimolecular mixture of this compound and $EnCH_3NH_2NO_2Cl_2PtCl$ is heated, there separates from solution not a mixture of crystals of the original compound, but a chemical compound of composition and properties corresponding to isomer I.

Found %: Pt 40.44
$EnCH_3NH_2NO_2ClBrPtCl$. Calculated %: Pt 40.40

Refractive-index measurements on samples of the salt obtained by the two methods gave agreeing results: $N_g = 1.75-1.76$; $N_p = 1.714$; extinction angle 45°.

Determination of the electrical conductivity of isomer I indicates that the compound forms two ions and undergoes far-reaching hydrolysis in the course of time.

On dilution ($t = 25°$)

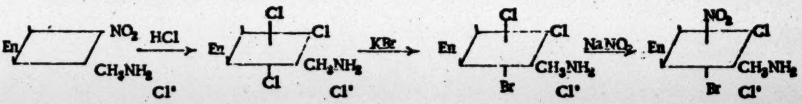
V — 1000	2000	4000 liter/mole
μ — 103.5	104.7	107.3 $\Omega^{-1}cm^2$

On reaction with water:

t (min)	$\mu(\Omega^{-1}cm^2)$	t(min)	$\mu(\Omega^{-1}cm^2)$
15	98.6	85	127.2
25	111.5	95	128.3
35	115.8	115	131.4
45	118.3	135	133.7
55	121.3	155	135.2
65	123.1	185	137.9
75	125.5	215	137.9
		245	140.9

II. Synthesis of $EnCH_3NH_2ClNO_2BrPtCl$ (Isomer II)

Trans-effect theory indicated a method of synthesis for isomer II similar to that used for the corresponding ammonia compound (I), namely:



The triammines $EnCH_3NH_2NO_2PtCl$ and $EnCH_3NH_2Cl_2PtCl$ have been described previously [4] and we prepared them by the methods given. It should be mentioned, however, that the first fractions of $FnCH_3NH_2Cl_3PtCl$ isolated from hydrochloric acid solution generally had a considerably elevated (by 5-6%) platinum content. Crystal-optical investigation of the product showed that it contained two phases, which could be separated by repeated crystallization. The admixed material was isolated as a white salt of composition $EnCH_3NH_2ClPtCl$.

Found %: Pt 54.72; Cl 20.11
$EnCH_3NH_2ClPtCl$. Calculated %: Pt 54.64; Cl 19.84.

It is evident that HCl reacts with $EnCH_3NH_2NO_2PtCl$ with complete destruction of the nitro group and formation of $EnCH_3NH_2ClPtCl$. The chlorine liberated when the nitro group is destroyed does not completely oxidize $EnCH_3NH_2ClPtCl$. Chlorination of the fraction of platinum content 50.66% led to the formation of the almost pure salt:

Found %: Pt 45.11
$EnCH_3NH_2Cl_3PtCl$. Calculated %: Pt 45.49.

In order to control the purity of $EnCH_3NH_2Cl_3PtCl$ the refractive indices of this compound and of the corresponding triammine of bivalent platinum were determined.

$EnCH_3NH_2Cl_3PtCl$	$EnCH_3NH_2ClPtCl$
Ng = 1.76	Ng = 1.685
Np = 1.712	Np = 1.598
Nm = 1.734	Nm = 1.664

It was essential for the performance of the next stage of synthesis – replacement of one of the chlorines on the coordinate Cl–Pt–Cl by bromine – that $EnCH_3NH_2Cl_3PtCl$ should be particularly pure. Otherwise side reactions would occur leading to formation of green compounds that greatly hinder the isolation of pure $EnCH_3NH_2Cl_2BrPtCl$. The same difficulty, though in appreciably lower degree, is met when the ammonia triammine $EnNH_3Cl_3PtCl$ is caused to react with potassium bromide.

The stereochemical reaction resulting in the formation of $EnCH_3NH_2Cl_2BrPtCl$ is analogous to the replacement of one chlorine by bromine in $EnCH_3NH_2NO_2Cl_2PtCl$. It is evident that here also the trans-dibromo compound formed, $EnCH_3NH_2ClBr_2PtCl$, reacts with unchanged $EnCH_3NH_2Cl_3PtCl$ molecules according to the equation:

$$EnCH_3NH_2ClBr_2PtCl + EnCH_3NH_2Cl_3PtCl \rightarrow EnCH_3NH_2Cl_2BrPtCl$$

Found %: Pt 41.02; 41.10; 41.21; Br 16.71; 16.42; Cl 23.05; 22.79.
$EnCH_3NH_2Cl_2BrPtCl$. Calc. %: Pt 41.30; Br 16.90 Cl 22.50

The most mobile chlorine in the molecule $EnCH_3NH_2Cl_2BrPtCl$ must be that situated on the same coordinate as the bromine. Treatment with a concentrated, slightly alkaline, cold solution of the calculated amount of sodium nitrite is followed fairly rapidly by the separation of a compound of composition corresponding fairly closely to $EnCH_3NH_2ClNO_2BrPtCl$.

Found %: Pt 39.40, 40.12, Br 18.36, Cl 13.60, Cl_{ion} 7.20, 7.04
$EnCH_3NH_2ClNO_2BrPtCl$. Calc. %: Pt 40.40, Br 16.56, Cl 14.67, Cl_{ion} 7.33

This triammine differs sharply in its properties from that of the same composition, but of configuration I; it is very similar to its ammonia analog $EnNH_3ClNO_2BrPtCl$; it is less soluble in water and is lighter in color than isomer I. Under the action of alkali, a proton readily splits from the methylamine group, yielding the amidodiammine $EnCH_3NHClNO_2BrPt$:

Found %: Pt 43.76, 44.10; Br 16.35; Cl 7.59; Br : Cl = 1 : 1.04.
$EnCH_3NHClNO_2BrPt$. Calculated %: Pt 43.69; Br 17.88; Cl 7.93.

Treatment of this with hydrochloric acid yields pure isomer II:

Found %: Pt 40.36; Br 16.80; Cl 14.40

Reprecipitation of the amido compound by addition of alkali to its solution in hydrochloric acid does not always lead to purification of the compound. Generally, the platinum content of the salt rises owing to partial splitting off of inner-sphere bromine in the alkaline medium and its replacement by chlorine.

Found %: Pt 45.41, 45.84; Br 8.64, 9.23; Cl 12.26, 11.96
$EnCH_3NHClNO_2BrPt$. Calculated %: Pt 43.69, Br 17.58, Cl 7.93

Because of these facts the reprecipitation of the amido compound in the experiments designed to separate the compound into its enantiomorphs was carried out from nitric acid solutions and the rotation was measured for the nitrate of the triammine.

Isomer II, unlike isomer I, slowly dissolves when treated with ammonia solution, but it was not found possible to isolate a tetrammine: the original salt remained in the solid phase. Also, it does not react with sodium nitrite, which is probably to be explained, as in the case of other triammines having an NO_2-Pt-X coordinate, by the ready reversibility of replacement reactions involving halogens standing opposite to the strongly trans-influencing nitro group.

Thus, the chemical properties of the triammine obtained, $[EnCH_3NH_2PtClBrNO_2]Cl$ corresponds to the configuration of isomer II, as it should do according to the method by which it was prepared. Refractive-index determinations gave the following results: $N_1 > 1.78$; $N_2 = 1.76$. Conductivity determinations showed that this compound of configuration I is only slowly hydrolyzed.

On dilution ($t = 25°$)

V = 500	1000	2000	4000 liter/mole
μ = 97.5	100.5	100.5	100.0 $\Omega^{-1}cm^2$

On reaction with water:

t (min)	μ, $\Omega^{-1}cm^2$	t(min)	μ $\Omega^{-1}cm^2$
25	98.1	105	104.3
35	100.9	135	104.3
45	101.3	165	104.7
55	102.1	205	105.9
75	102.7	235	106.7

III. Separation of $EnNH_3ClNO_2BrPtCl$ into its Enantiomorphs

The separation was effected by crystallization of the triammine in the form of its hydrogen tartrate. The theoretically calculated amount (2.322 g) of $Ag_2C_4H_4O_6$ was added to a solution of $EnCH_3NH_2ClNO_2BrPtCl$ (6 g) in water (146 ml). AgCl was separated, and the amount of tartaric acid calculated for the formation of the hydrogen tartrate (0.95 g) was added. The salt began to crystallize after two weeks, when the solution attained a concentration of 20% with respect to the triammine hydrogen tartrate.

Fraction I of the crystals (2.1 g) was a light yellow, finely crystalline substance of low solubility in cold water. The configuration of the less soluble combination was (++).

Found %: Pt 32.86
$EnNH_3ClNO_2BrPtC_4H_5O_6$ Calculated%: Pt 33.51.

The hydrogen tartrate was dissolved in a 1% solution of HCl and then treated with an excess of alkali. The amido compound that separated was filtered off, washed with cold water, and reprecipitated from hydrochloric acid solution.

Found %: Pt 44.86, 44.91.
$EnNH_2ClNO_2BrPt$. Calculated%: Pt 45.13

After the second precipitation of the amido compound, the filtrate showed no rotation.

Determination of the Rotation of d-$EnNH_3ClNO_2BrPtCl$ (Fraction 1).

Weight of amido compound 0.2227 g; V = 13 ml H_2O containing an excess of HCl; $\underline{l} = 1.5$ dm; $c_{chloride} = 1.85$; $\alpha_C = +0.05°$; $\alpha_D = +0.08°$; $\alpha_E = +0.11°$; α_F—this could not be determined owing to the high light absorption.

$$\alpha_E/\alpha_C = 2.20;\ [\alpha]_D = +2.92°;\ [M]_D = +13.69°.$$

It was not found possible to measure the rotation of the amido compound at this concentration: it separated out into the solid phase. We therefore had recourse to further dilution: 5 ml of the solution of the chloride (c = 1.85) was brought in alkaline solution up to a volume of 13 ml.

Determination of the Rotation of l-$EnNH_2ClNO_2BrPt$ (Fraction I).

$c = 0.57$, $\underline{l} = 1.5$ dm; $\alpha_C = -0.06°$; $\alpha_D = -0.10°$, $\alpha_E = -0.13°$.

$$\alpha_E/\alpha_C = 2.16;\ [\alpha]_D = -11.69°;\ [M]_D = -50.56°;\ \rho = 3.69.$$

Fairly rapid racemization occurs in alkaline solution: the rotation was reduced to nil by the next day.

Fraction II of the crystals (0.56 g) was filtered off three days after the separation of Fraction I. In platinum content it corresponded to the normal tartrate crystallizing with one-half a molecule of tartaric acid.

Found %: Pt 35.96; 36.07.
$(EnNH_3ClNO_2BrPt)_2C_4H_4O_6 \cdot \frac{1}{2}C_4H_4O_6$. Calculated%: pt 35.81.

The amido compound precipitated from this portion of the tartrate appeared to be pure and, in view of the small amount, was not reprecipitated. Pt found: 45.28%. Its chloride gave dextro rotation equal to that of the chloride of Fraction I.

Determination of the Rotation of d-$EnNH_2ClNO_2BrPtCl$ (Figure II).

Amido compound, 0.3059 g; V = 17.50 ml H_2O containing 0.24 ml HCl (1:3); c = 1.89; l = 2.4; α_C = +0.10°; α_D = + 0.14°; α_E = + 0.21°.

$$\alpha_E / \alpha_C = 2.10;\ [\alpha]_D = +3.02°;\ [M]_D = +14.15°.$$

Determination of the rotation of l-$EnNH_2ClNO_2BrPt$ (Fraction II).

Caustic soda (10%, 0.27 ml) was added to the solution of the chloride; l = 2.4 dm; c = 1.71; α_C = 0.53°; α_D = −0.80°; α_E = −1.07°; α_E/α_C = 2.02; $[\alpha]_D$ = −19.09°; $[M]_D$ = −82.58°; p = 5.83.

The agreement between the results of the rotation determinations for chloride from the two fractions of configuration (++) may be considered to be within the limits of experimental error. The divergence in the values of $[M]_D$ for the amido compound is to be explained by the inactivation of the compound in an alkaline medium, which proceeded to an appreciable extent during the dilution operation carried out on the solution of the amido compound of Fraction I.

The first two fractions comprised about one-third of the ammine hydrogen tartrate that could be formed from the chloride. Fraction III was filtered off two days after Fraction II (1.5 g). We did not succeed in measuring the rotation of the chloride, the angles being so small. However, the amido compound showed a definite levo rotation. From the mother liquor, after separation of Fraction III, the amido compound of Fraction IV (1.2 g) was separated by the action of alkali.

Found %: Pt 44.98.
$EnNH_2ClNO_2BrPt$. Calculated %: Pt 45.13.

For fear that it might undergo rapid racemization in alkaline solution, the amido compound was not reprecipitated: it was converted by the action of a small excess of hydrochloric acid into the chloride. Part of the chloride separated immediately from the solution (Fraction IVa), and a second fraction was separated after two days (Fraction IVb).

Found %: Pt 41.82, 41.44.
$EnNH_3ClNO_2BrPtCl$. Calculated %: Pt 41.62.

Both chloride fractions showed levo rotation.

Determination of the Rotation of l-$EnNH_3ClNO_2BrPtCl$ (Fraction IVa).

Chloride, 0.4625 g; V = 13 ml; c = 3.55; l = 1.5 dm; α_C = −0.09°; α_D = −0.15°; α_E = −0.20°; α_E/α_C = 2.22; $[\alpha]_D$ = −2.81°; $[M]_D$ = −13.18°.

The molecular rotation of the levo enantiomorph was 93% of the rotation of the dextro enantiomorph, which indicates an adequate completeness of separation.

Addition of alkali to a solution of the chloride (c = 3.55) caused reversal of the sign of the rotation, but it was not possible to measure the rotation owing to the precipitation of the amido compound. The measurement was carried out with amido compound at a twofold dilution.

Determination of the Rotation of d-$EnNH_2ClNO_2BrPt$ (Fraction IVa).

l = 1.5 dm; c = 1.63; α_C = + 0.25°; α_D = + 0.37°; α_E = + 0.50°; α_E/α_C = 2.00; $[\alpha]_D$ = + 13.90°; $[M]_D$ = + 56.61°; ρ = 4.29. After acidification with hydrochloric acid, the solution lost its activity completely after two days; $[\alpha_D]$ = −0.37°; $[M]_D$ − 1.73°, consequently the process of inactivation proceeds also in acid medium, although more slowly than in alkaline.

Determination of the Rotation of l-$EnNH_3ClNO_2BrPtCl$ (Fraction IVb).

Chloride, 0.1624 g; V = 13.0 ml; l = 1.5 dm; c = 1.25; α_C = −0.03°; α_D = −0.04°; α_E = −0.06°; α_F = −0.11°; α_E/α_C = 2.00; α_F/α_C = 3.66; $[\alpha]_D$ = −2.13°; $[M]_D$ = −9.99°.

Determination of the Rotation of d-$EnNH_2ClNO_2BrPt$ (Fraction IVb) (without further dilution).

l = 1.5 dm; V = 13.0 ml of chloride solution + 0.3 ml 10% KOH; c = 1.12; α_C = + 0.17°; α_D = + 0.23°; α_E = 0.34°; $\alpha_F \approx 0.63°$; α_E/α_C = 2.00; α_F/α_C = 3.70; $[\alpha]_D$ = + 1.37°; $[M]_D$ = + 59.26°; ρ = 5.92.

The amido-inversion coefficient from Fraction IVb agrees well with the value from Fraction II of the dextro enantiomorph, for which the measurement of the rotation of the amido compound was carried out rapidly without further dilution. Admixture of racemate to this fraction of chloride should not affect the optical-activity coefficients.

IV. Separation of $\mathrm{EnCH_3NH_2ClNO_2BrPtCl}$ into its Enantiomorphs

The triammine was separated into its enantiomorphs by crystallization in the form of the ammine hydrogen tartrate.

Experiment No. 1. To a solution of the chloride (3.3558 g), $\mathrm{Ag_2C_4H_4O_6}$ (1.2631 g) and tartaric acid (0.5208 g. amount calculated for formation of the hydrogen tartrate) were added. The solution had a concentration of 10-15% with respect to ammine hydrogen tartrate. After considerable evaporation of the solution, a first fraction of well-formed crystals (1.28 g) corresponding in composition to the hydrogen tartrate was obtained. The configuration of the difficultly soluble combination was (++).

Found %: Pt 32.30

$\mathrm{EnCH_3NH_2ClNO_2BrPtC_4H_5O_6}$. Calculated %: Pt 32.71

From this fraction, a double reprecipitation from a 1% solution of nitric acid yielded the amido compound.

Found %: Pt 43.54

$\mathrm{EnCH_3NHClNO_2BrPt}$. Calculated %: Pt 43.69

Measurement of the Rotation of d-$\mathrm{EnCH_3NH_2ClNO_2BrPtNO_3}$ (Fraction I). The amido compound (0.3232 g) was dissolved in water (13 ml) containing $\mathrm{HNO_3}$ (1:3) (0.21 ml); l = 2.3 dm; c = 2.04; $\alpha_C = +0.08°$; $\alpha_D = +0.08°$; $\alpha_E = +0.12°$; $\alpha_E/\alpha_C = 1.5$; $[\alpha]_D = +1.70°$; $[M]_D = +8.68°$.

An excess (2 ml) of 10% KOH was added to the solution of the nitrate.

Measurement of the rotation of l-$\mathrm{EnCH_3NHClNO_2BrPt}$ (Fraction I).

V = 20 ml; l = 1.5; c = 1.616; $\alpha_C = -0.15°$; $\alpha_D = -0.24°$; $\alpha_E = -0.32$; $\alpha_E/\alpha_C = 2.13$; $[\alpha]_D = -9.90°$; $[M]_D = -44.32°$: $\rho = 5.09$. The rotation of the alkaline solution had disappeared by the next day.

Further evaporation of the mother liquor after separation of the Fraction I crystals of the hydrogen tartrate led to formation of a sticky mass. By repeated dissolution and evaporation it was found possible to separate one further fraction of crystals. The amido compound obtained from them showed a very feeble rotation in acid medium, which it was not found possible to measure, but a definite dextro rotation was observed in alkaline medium. When alkali was added to the mother liquor after separation of Fraction II, no amido compound separated. We therefore did not succeed in obtaining the second enantiomorph.

As the results of the first experiment were somewhat unexpected – the difficultly soluble combinations of the ammonia and the methylamine triammines had the same configuration – we carried out a repeat experiment on the separation of $\mathrm{EnCH_3NH_2ClNO_2BrPtCl}$ in the form of its hydrogen tartrate.

Experiment No. 2. The amido compound $\mathrm{EnCH_3NHClNO_2BrPt}$ (4.0157 g) was dissolved in water (70-80 ml) containing the calculated amount (1.3488 g) of tartaric acid. After six days well-formed light yellow crystals (1.9 g) of the hydrogen tartrate separated from the solution.

Found %: Pt 33.09

$\mathrm{EnCH_3NH_3ClNO_2BrPtC_4H_5O_6}$. Calculated %: Pt 32.71.

The amido compound was obtained from Fraction I of the hydrogen tartrate by double reprecipitation. Its solution in nitric acid showed dextro rotation, the value being in accord with the results of the first experiment.

Measurement of the Rotation of d-$\mathrm{EnCH_3NH_2ClNO_2BrPtNO_3}$ (Fraction I).

The amido compound (0.4631 g) was dissolved in water (18 ml) containing $\mathrm{HNO_3}$ (1:3) (0.30 ml); c = 2.92; l = 2.3 dm; $\alpha_C = +0.10°$; $\alpha_D = +0.12°$; α_E 0.13°; $\alpha_E/\alpha_C = 1.30$; $[\alpha]_D = +1.78°$; $[M]_D = +9.05°$

By the action of alkali (0.1 ml of 10% KOH) the sign of rotation was reversed: V = 19 ml; c = 2.43; l = 2.3 dm; $\alpha_C = -0.27°$; $\alpha_D = -0.30°$; $\alpha_E = -0.53°$; $\alpha_E/\alpha_C = 1.96$; $[\alpha]_D = -7.15°$; $[M]_D = -32.01°$; $\rho = 3.53$; Owing to the strong absorption of the solution, the measurements were repeated at l = 1.5 dm: $\alpha_C = -0.21°$; $\alpha_D = -0.29°$; $\alpha_E = -0.38°$; $\alpha_E/\alpha_C = 1.80$; $[\alpha]_D = -7.92°$; $[M]_D = -35.38°$: = 3.20.

When an excess of alkali (2 ml) was added, the rotation coincided with the results for the rotation of the amido compound in Experiment No. 1: $V = 20$ ml; $c = 2.31$; $\underline{l} = 1.5$ dm; $\alpha_C = -0.35°$; $\alpha_D = -0.54°$; $\alpha_E = -2.16°$; $[\alpha]_D = -10.10°$; $[M]_D = -45.22°$; $\rho = 4.99$.

As in Experiment No. 1, it was not found possible to isolate the levo enantiomorph. However, the fairly good agreement between the absolute values of the rotation and coefficients of rotation for the dextro enantiomorph in the two experiments indicates that it is of high purity.

We take this opportunity of expressing our thanks to E.E. Burovaya and V. M. Ezuchevskaya for carrying out crystal-optical determinations and electrical-conductivity measurements on the compounds prepared.

SUMMARY

1. Two geometric isomers of the methylamine triammine of composition $[EnCH_3NH_2PtClBrNO_2]Cl$, and of structure $EnCH_3NH_2NO_2ClBrPtCl$ and $EnCH_3NH_2ClNO_2BrPtCl$ respectively have been prepared.

2. It has been shown that replacement of ammonia by methylamine in $[EnAmPtClBrNO_2]Cl$ does not have any appreciable effect on the course of the synthesis and on the chemical properties of the isomeric triammines.

3. Ammonia and methylamine triammines of identical structure – $EnNH_2ClNO_2BrPtCl$ and $EnCH_3NH_2ClNO_2BrPtCl$ – have been separated into their enantiomorphs. Measurements have been made of the values of the rotations and dispersions of the compounds $\underline{d}(\underline{l})$-$EnH_2ClNO_2BrPtCl$ and $\underline{l}(\underline{d})$ $EnNH_2ClNO_2BrPt$, $\underline{d}$-$EnCH_3NH_2ClNO_2BrPtNO_3$ and $\underline{l}$-$EnCH_3NHClNO_2BrPt$.

4. It has been shown that the configuration of the difficultly soluble combination for the two triammine hydrogen tartrates is identical (++), which is the reverse of the position found for the analogous dichloronitrotriammines.

5. It has been found that the amido-inversion coefficients ρ for the reactions

$$EnNH_2ClNO_2BrPtCl \underset{HCl}{\overset{KOH}{\rightleftarrows}} EnNH_2ClNO_2BrPt$$

and

$$EnCH_3NH_2ClNO_2BrPtNO_3 \underset{HNO_3}{\overset{KOH}{\rightleftarrows}} EnCH_3NHClNO_2BrPt$$

are very close in value, on the average about 6 for the first and about 5 for the second reaction; this behavior contrasts with that of the dichloronitrotriammines, for which ρ rises from 4-6 for the ammonia triammine to 21-29 for the methylamine triammine.

6. It has been shown that the rotatory power of the methylamine triammine is lower than that of the ammonia triammine.

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THERMOCHEMICAL INVESTIGATION OF ISOMERIC PLATINUM COMPOUNDS

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Thermochemical investigation of complex platinum compounds, particularly isomeric compounds, is capable of yielding material for the characterization of the energetics of the trans effect. A number of investigations has been devoted to the study of the isomeric changes of complex compounds of the platinum metals. Chugaev and Pshenitsyn [1] have established that the green salt $[Pt(NH_3)_4][PtCl_4]$, on being heated carefully at near the decomposition temperature, undergoes depolymerization to the trans monomer $[Pt(NH_3)_2Cl_2]$. In connection with this work it should be noted that as early as 1841 Fehling [2] showed that the salt $[Pd(NH_3)_4][PdCl_4]$, on being heated to 200°, underwent a similar change. An attempt to determine the difference in total energy between the cis and trans nitrites of platinum by estimating their heats of combustion in a calorimetric bomb, which was made in 1931 [3], was not successful; it was found that the heats of combustion of the cis and trans nitrites were identical, within the limits of experimental error.

Investigations into the thermal stability of complex compounds of platinum and the platinum metals, which were carried out by Grinberg, Ptitsyn, Nikolaev, and Rubinshtein [4,5,6], showed that trans isomers are generally more stable than the corresponding cis isomers. Measurements [7] have shown that the specific heats of the cis- and trans-dichlorodiammineplatinums are identical between 20° and 50°.

The present work is devoted to the determination of the difference in total energy between the isomeric chloroammines of bivalent platinum on the basis of measurements of the heats of reaction of these isomers with aqueous ammonia.

It is known that the difficultly soluble isomeric chloroammines of bivalent platinum react on being heated with aqueous ammonia to 70-80° to give a solution of tetrammineplatinum (II) chloride, a compound that has no isomers. Hence the difference between the heats of reaction of the isomers with ammonia is a direct measure of the difference of the total energies of the isomers.

In choosing the method of investigation it was necessary to take the following points into account: 1) the difference between the total energies of the isomers is determined in the form of a small difference between two relatively large numbers - heats of reaction, which are directly measured; 2) the measurements of the heats of reaction have to be carried out at elevated temperatures (70-80°) in a volatile solvent; 3) the reactions studied may have a comparatively low rate; 4) it is desirable that it should be possible to work with small amounts of the salts.

EXPERIMENTAL

Apparatus and Method of Measurement

We constructed a hermetic calorimeter (for liquids) having constant heat exchange (adiabatic) and permitting the measurement of small amounts of heat for slow-running processes at temperatures ranging from room temperature to 100-120°. The calorimeter is in many ways similar to that constructed by Kiselev [8] for the measurements of heats of adsorption.

The general scheme of the arrangement is shown in the figure. (See plate, page 195). The calorimetric unit consists of the calorimeter 1, the liquid jacket 2, and arrangements for the regulation and measurement of temperature. The calorimeter itself, 1, consists of an inner thin-walled beaker, about 250 ml in volume, placed on a textolite stand in a thin-walled outer beaker, which is hermetically closed with a cover. The inner and outer beakers and the cover are made of stainless steel. The calorimeter is fixed in the center of the jacket by the aid of five tubes of stainless steel screwed into the cover of the outer beaker; through these pass the leads of the resistance thermometers, the axis of the stirrer, and an arrangement for breaking the ampoule containing the substance under investigation. The jacket 2 is a cylindrical vessel, volume about 30 liters, filled with a mixture (1:1) of transformer oil and kerosene. Stirring in the jacket is effected by means of a propeller stirrer situated in the tube 3.

The changes in temperature in the calorimeter are measured by a platinum resistance thermometer, resistance about 127 ohms at 70°, and a bridge. Two arms of the equal-arm Wheatstone bridge 4 consist of ten-ohm resistances; the thermometer in the calorimeter and a constant resistance of 127 ohms form the other two arms of the bridge. In parallel with the 127-ohm coil is a precision six-dialed resistance box, which serves for the maintenance of the balance of the bridge and allows measurements to be made of the change in resistance of the thermometer with change in temperature. A mirror galvanometer having a period of three seconds and a p.d.-sensitivity of 1 mm/m $\approx 6 \cdot 10^{-8}$ V is placed in the diagonal of the bridge. The equilibrium of the bridge is controlled by the aid of a viewing tube and scale, which is placed at a distance of six meters from the galvanometer. The arrangement described permits a thermometric sensitivity of about $5 \cdot 10^{-6}$.

The heat equivalent of the calorimeter is determined after each experiment and is, in effect, a measurement of the work done by the current in heating the calorimeter. For this purpose there is a heater of resistance about 13 ohms in the calorimeter. In order to determine the current strength, the differences of potential between the ends of the heater and of the standard 10-ohm resistance are measured with a compensator. The time is determined by the aid of a Gipp chronoscope.

The temperature of the jacket is controlled automatically, and for this purpose the Wheatstone bridge 5 and the photo-relay 6 are used. The bridge is composed of two constant resistances, each of 10 ohms, and two platinum resistance thermometers. One of the control resistance thermometers is placed in the calorimeter, and the other is placed in the jacket. Each control thermometer has a resistance of about 130 ohms at 70°. A mirror galvanometer, similar to the one already mentioned, is placed in the diagonal of the control bridge. The measuring and control Wheatstone bridges are supplied with a current of 0.1 amp from accumulators, and during an experiment this current is maintained constant within $5 \cdot 10^{-8}$ mA.

Measurements were carried out of the heats of reaction of isomeric chloroammines of bivalent platinum with aqueous ammonia (9.4%) at 70°. Of a group of seven isomeric chloroammines of bivalent platinum, five were investigated: two monomers – cis-$[Pt(NH_3)_2Cl_2]$ and trans-$[Pt(NH_3)_2Cl_2]$, the dimer $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ and two trimers – $[Pt(NH_3)_3Cl]_2[PtCl_4]$ and $[Pt(NH_3)_4][PtNH_3Cl_3]_2$. All the enumerated isomers have the empirical composition $PtCl_2 2NH_3$. Owing to the specific behavior of the pink and green salts $[Pt(NH_3)_4][PtCl_4]$ in ammoniacal solution (the spontaneous change of the pink salt into the green and the very slow dissolution of the latter), only preliminary results were obtained for these salts, and these are not given here.

The salts employed were synthesized from spongy platinum and were carefully purified. Crystal-optical and chemical analyses showed that the salts prepared contained no impurities. The reactions proceeding in the calorimeter may be written in the following general form:

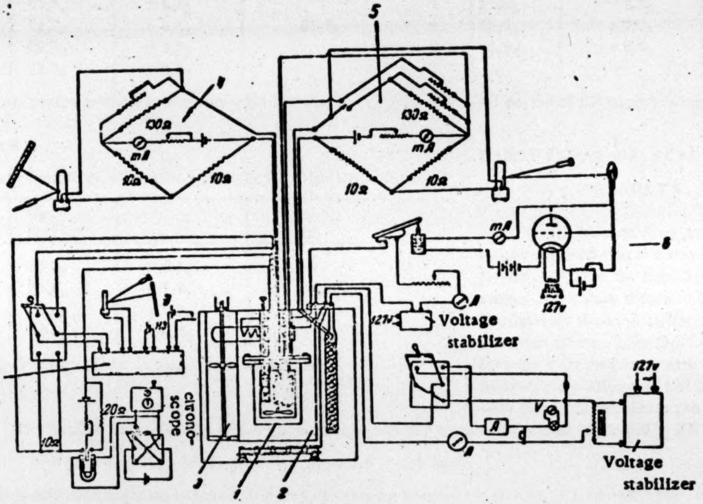
$$nPtCl_2 \cdot 2NH_3 + 2nNH_3 = n[Pt(NH_3)_4]Cl_2 + Q,$$

where n = 1,2 or 3. The quantities taken in all experiments were: ammonia solution, 210.0 g; salt, 0.3000 g.

The results of heat-of-reaction measurements for the five isomeric chloroammines of bivalent platinum are given in Tables 1-6. The values of Q in the second column of the tables are heats measured in the calorimeter. In the third column the departures of the measurements from the mean are given. In the fourth column the mean values of the measured heats are given.

It should be pointed out that the values of Q given in the tables contain a systematic error of about 7 cal/g. This error is associated with the presence of air in the ampoule containing the substance. When the ampoule was crushed, this "air bubble" became saturated with ammonia. The value of the thermal effect due to the "air bubble" was estimated in special experiments, and it was found to be sufficiently constant for ampoules of the volume employed. The difference of the measured heats for two isomers, without correction for the air bubble, gives the heat of isomerization (the difference in the total energies of the isomers), since the bubble effect is excluded at the same time.

The quantity Q_p, corrected for the "bubble effect", gives the heat of reaction of the salt with the ammonia solution. The error in this quantity is made up of the error in the measurement of Q and the error in the measurement of the "bubble effect." The values of the heats of reaction of isomeric platinum compounds with ammonia presents interest for its own sake, for from these, by the use of data in the literature, it is possible to calculate the heats of formation of the isomers. However, the data in the literature are given for a standard temperature (25°). As the specific heats of the compounds investigated are not known, it was possible to make only approximate calculations of the heats of reaction at 25° and to determine heats of formation of the isomers at this standard temperature.


5
4
130Ω
mA
10Ω
10Ω
130Ω
mA
10Ω
10Ω
6
mA
127v
A
127v
Voltage stabilizer
V
A
A
127v
Voltage stabilizer
3
H3
Ealon com-pensator
20Ω
10Ω
crono-scope
3
1
2

General diagram of apparatus.

TABLE 1

Heat of reaction Q_1 of cis-$[Pt(NH_3)_2Cl_2]$ with NH_3 solution;

Expt. No.	Q_1 (cal/g)	$Q_1 - \bar{Q}_1$	$\bar{Q}_1$
1	62.5_1	$+0.13_8$	
2	61.9_4	-0.43_2	62.3_7
3	62.3_2	-0.05_2	
4	62.7_3	$+0.35_8$	

Principal period of the experiments 4-5 minutes

TABLE 2

Heat of reaction Q_2 of trans-$[Pt(NH_3)_2Cl_2]$ with NH_3 solution.

Expt. No.	Q_2 (cal/g)	$Q_2 - \bar{Q}_2$	$\bar{Q}_2$
1	52.1_8	$+0.02_5$	
2	52.1_5	-0.00_5	52.1_{55}
3	52.1_9	$+0.03_5$	
4	52.1_0	-0.05_5	

Principal period of the experiments ~ 4 minutes.

TABLE 3

Heat of reaction Q_3 of $[Pt(NH_3)_3Cl][PtNH_3Cl_3]$
with NH_3 solution

Expt. No.	Q_3 (cal/g)	$Q_3 - \bar{Q}_3$	$\bar{Q}_3$
1	61.6_6	-0.1_1	
2	62.2_2	$+0.4_5$	61.7_7
3	62.5_2	-0.2_5	
4	61.7_0	-0.0_7	

Principal period of the experiments ~ 3.5 minutes

TABLE 4

Heat of reaction Q_4 of $[Pt(NH_3)_3Cl]_2[PtCl_4]$ with
NH_3 solution

Expt. No.	Q_4 (cal/g)	$Q_4 - \bar{Q}_4$	$\bar{Q}_4$
1	54.8_3	-0.1_0	
2	55.0_4	$+0.1_1$	54.9_3
3	54.9_4	$+0.0_1$	

Principal period of the experiments ~ 20 minutes

TABLE 5

Heat of reaction Q_5 of $[Pt(NH_3)_4][PtNH_3Cl_3]_2$ with NH_3 solution

Expt. No.	Q_5 (cal/g)	$Q_5 - \bar{Q}_5$	$\bar{Q}_5$
1	58.3_3	-1.1_4	
2	60.6_7	$+1.2_0$	59.4_7
3	59.8_2	$+0.3_5$	
4	59.0_8	$+0.3_9$	

Principal period of the experiments ~ 18 minutes

DISCUSSION OF EXPERIMENTAL RESULTS

It will be seen from an examination of the results obtained that the trans monomer $[Pt(NH_3)_2Cl_2]$ has the least heat of reaction with ammonia. It may therefore be supposed that it is relatively the most stable isomer, i.e., all of the other isomers investigated should go over into the trans monomer with evolution of heat. By taking the differences of the heats of reaction with ammonia we obtain the heats of isomerization. The heat of isomerization of the cis monomer into the trans monomer at 70° is 3.0 ± 0.2 kcal/mole.

$$\text{cis-}[Pt(NH_3)_2Cl_2] \rightarrow \text{trans-}[Pt(NH_3)_2Cl_2] + 3.0 \pm 0.2\ \text{kcal}$$

This isomerization reaction has been effected directly by heating cis-$[Pt(NH_3)_2Cl_2]$ to 170° [6].

The following isomerization (depolymerization) reactions may be predicted, the heats of reaction being obtained from our measurements (at 70°):

$$[Pt(NH_3)_3Cl]\,[PtNH_3Cl_3] \rightarrow 2(NH_3)_2Cl_2Pt \quad + 5.8 \pm 0.3\ \text{kcal;}$$

$$[Pt(NH_3)_3Cl]_2[PtCl_4] \rightarrow 3(NH_3)_2ClPt \quad + 2.5 \pm 0.3\ \text{kcal;}$$

$$[Pt(NH_3)_4][PtNH_3Cl_3]_2 \rightarrow 3(NH_3)_2Cl_2Pt \quad + 6.6 \pm 1.2\ \text{kcal.}$$

SUMMARY

1. A method has been proposed for the determination of the differences between the total energies of isomeric platinum chloroammines.

2. A hermetic calorimeter for liquids, having constant heat exchange and permitting measurements to be taken from room temperature to 100-120°, has been constructed. The thermometer of the calorimeter has a sensi-

tivity of the order of $5 \cdot 10^{-6}$. The calorimetric sensitivity of the apparatus is $1.5 \cdot 10^{-7}$ cal. The amount of complex compound required for the measurement is 0.1 - 0.3 g.

3. Measurements have been made of the heats of reaction of five chloroammines of bivalent platinum with aqueous ammonia (9.4% NH_3) at 70°, the probable error being about 1%. The heats of four isomeric changes have been estimated (probable error about 10%).

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COMPLEX COMPOUNDS OF PLATINUM WITH ACETAMIDE

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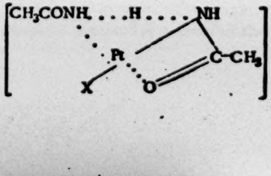
One of the peculiarities of nonionic platinum-acetamide complexes of the form $[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot X]$ where $X = NO_3$, Cl, Br, I, CNS, or NO_2, is, as we have already pointed out [1], the notable difference in character between the linkage of the platinum with the two acetamide groups and that formed with the acidic addend. The latter, in spite of the evident complex nature of its bond with platinum, is very mobile and is comparatively readily replaced by various acidic atoms and groups, while at the same time all the original properties characteristic of platinum acetamide compounds remain unchanged. In contrast to the acid addend, the acetamide molecule and the acetamido group are firmly bound to the platinum, and furthermore, the acetamide groups appear to be inseparably attached to one another. When various chemical reagents react with the compound, either the grouping comprised of an acetamide molecule and an acetamido group remains unchanged, or the two groups are eliminated together, leading to formation of the usual platinum complex compounds. In spite of many attempts, it has not been found possible to replace any one of the acetamide groups by another addend. This peculiarity in the chemical behavior of the addends of platinum acetamide compounds opens up wide possibilities for the synthesis of compounds having various acidic addends. However, all the compounds are characterized by remarkable stability to such powerful oxidizing agents as aqua regia, gaseous chlorine, bromine, concentrated nitric acid, and so on. In contrast to all other known complex compounds of bivalent platinum, in this case oxidation of the platinum does not occur, and the reaction leads only to the replacement of one acidic addend by another, without any change in the acetamide grouping, i.e., conversion of one acetamide compound into another occurs.

This reaction, which has no parallel in the chemistry of the complex compounds of bivalent platinum, allows us to suppose that the anomalous properties of platinum acetamide compounds depend to a considerable extent on the acetamide grouping, firmly bound to platinum. The remarkable stability of this grouping is brought out particularly clearly in the reaction between platinum acetamide compounds and concentrated nitric acids. Only by long and intensive boiling with concentrated acid (sp. gr. 1.41) is it possible to bring these substances into solution, and from the solution, cooled and diluted with water, a nitratoamidoamideplatinum separates. If the precipitate is immediately filtered off and an agent such as HCl, NH_4Br, NH_4CNS or $NaNO_2$ is added to the filtrate, then a precipitate of chloro-, cromo-, thiocyanato-, or nitro-amidoamideplatinum separates fairly rapidly. Such a course of reaction is in full accord with the low coordinating power of the group NO_3, which shows a greater mobility in a nitratoamidoamideplatinum than any of the other acidic addends, and is particularly readily replaced.

It was by this method that we synthesized a bromoamidoamideplatinum of homogeneous composition, which has not been done previously by the usual method (action of KBr on chloroamidoamideplatinum). The properties and chemical behavior of the bromoamidoamideplatinum not only confirm the far-reaching analogy of this compound with all other nonionic acetamide compounds, but also allow us to place it, on the basis of its reactivity, between the chloro- and iodo-amidoamideplatinums in the series of these compounds. Actually, if we arrange acetamide platinum compounds according to their reactivities, we obtain a kind of natural series, at the extremes of which are found compounds containing NO_3 and NO_2. All the remaining compounds follow one after the other in order of decreasing or increasing coordinating power, or of the magnitudes of the trans effects of the corresponding acidic addends: NO_3, Cl, Br, I, CNS, and NO_2.

Thus, on the basis of the experimental results we may conclude that the greater the trans effect and coordinating power of an acidic addend, the less the reactivity of the corresponding nonionic acetamide platinum compound and the greater its stability. To what extent this relation is a manifestation of the trans-effect principle can only be determined on the basis of a thorough and careful study of the chemical nature of platinum acetamide compounds. Further study of the chemical nature of these compounds is essential also for the elucidation of the reasons for their anomalous properties, for the proposed structure of these compounds, which is expressed by the formula



where X = NO_3, Cl, Br, I, CNS, or NO_2, cannot explain all their peculiarities in behavior. However, the direct study of nonionic compounds is rendered difficult by their exceptionally poor solubility, and it has consequently been necessary to have recourse to electrolyte types. The synthesis of such compounds is of particular interest also for the solution of the question whether the anomalous properties of the compounds discussed above are peculiar to the nonelectrolyte type, or are preserved also in ionic compounds of good solubility.

EXPERIMENTAL

Reaction of Platinum Acetamide Compounds with Ethylenediamine

A classical method for the preparation of ionic bivalent platinum compounds consists in treating nonelectrolytes with amines [2]. The reaction may lead to the formation of compounds containing from one to four molecules of amine, according to the number of amine molecules introduced into the inner sphere of the complex compound. As far as platinum acetamide compounds are concerned, certain peculiar properties, in particular the presence of a readily replaceable acidic addend in the inner sphere, encourage replacement by the amine of this addend. Particular interest is presented by the question whether the stability, characteristic of platinum acetamide compounds, of the acetamido-acetamide grouping and their mutual linkage will be preserved in this reaction, or will it be possible, by the use of an amine such as ethylenediamine, to replace one of the acetamides? In view of these problems, ethylenediamine and ammonia were employed in the investigation. Previous experiments had shown that, in the cold, ethylenediamine does not react appreciably with platinum acetamide compounds of the nonionic type, while strong heating leads to elimination of both acetamide molecules with formation of platinum ethylenediamine compounds. It was necessary to try to find intermediate conditions under which there was a chance of the formation of mixed ethylenediamine-acetamide platinum compounds. As a result of a large number of experiments, such conditions were found, and ethylenediamine-acetamide compounds of platinum were isolated in the form of pale-yellow, finely crystalline precipitates. It should be noted that, in spite of the great similarity in properties and behavior of the initial platinum acetamide compounds, their individual character is manifest also in their reactions with ethylenediamine.

In full accord with its high reactivity, the nitratoamidoamideplatinum readily dissolved when warmed slightly with an aqueous solution of ethylenediamine, taken in slight excess over equimolecular quantities. When insufficient ethylenediamine was taken, then on evaporation of the solution separation of some of the original nitratoamidoamideplatinum was observed. All the remaining platinum acetamide compounds dissolved only after long heating with ethylenediamine solutions. It is recommended that a great excess of ethylenediamine should be avoided, as it leads to formation of ethylenediamine compounds of formula $[PtEn_2]X_2$, where X = Cl, Br, I, or CNS.

We give here the analytical results on compounds prepared by the action of ethylenediamine on 1) the chloroamidoamideplatinum, 2) the nitratoamidoamideplatinum, 3) the bromoamidoamideplatinum, 4) the iodoamidoamideplatinum, 5) the thiocyanatoamidoamideplatinum, and 6) the nitroamidoamideplatinum:

$[PtNH_2COCH_3NHCOCH_3En]Cl$.
1. Found %: Pt 47.54; 48.38; Cl 8.86; 8.40
Calculated %: Pt 47.89; Cl 8.74

$[PtNH_2COCH_3NHCOCH_3En]NO_3$.
2. Found %: Pt 45.24; 44.50; N 15.40
Calculated %: Pt 44.93; N 16.12

$[PtNH_2COCH_3NHCOCH_3En]Br$.
3. Found %: Pt 43.81; 42.99; Br 18.65
Calculated %: Pt 43.14; Br 17.73

$[PtNH_2COCH_3NHCOCH_3En]I$.
4. Found %: Pt 38.36; 39.27; 39.29
Calculated %: Pt 39.07

$[PtNH_2COCH_3NHCOCH_3En]CNS$.
5. Found %: Pt 45.12; 45.87
Calculated %: Pt 45.34

$[PtNH_2COCH_3NHCOCH_3En]NO_2$.
6. Found %: Pt 47.11; N 16.20; 16.60
Calculated %: Pt 46.65; N 16.74

On the basis of the analytical results on the compounds obtained it may be supposed that in the reaction of ethylenediamine with nonionic platinum acetamide compounds the ethylenediamine is taken into the inner sphere and the acidic addends are displaced into the outer sphere, as indicated by the following equation:

$$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot X] + En \longrightarrow [PtNH_2COCH_3 \cdot NHCOCH_3 \cdot En]X,$$

where X = NO_3, Cl, Br, I, CNS or NO_2.

In spite of the great tendency of ethylenediamine to occupy two coordination places with formation of a stable five-membered ring, in the present case it evidently occupies only one coordination position, and the acetamido-acetamide grouping is preserved unchanged. However, this question cannot be regarded as resolved, for some properties of the compounds obtained do not support this conclusion.

Thus, the presence of a free amino group in these compounds should be shown by an alkaline reaction in aqueous solution and increased electrical conductivity, but the solutions have a neutral reaction and the values of the conductivity are characteristic for typical two-ion electrolytes. We give here the results of conductivity determinations for these compounds; they were kindly carried out by V. M Izuchevskaya.

Electrical conductivity of aqueous solutions of the amido(ethylenediamine)amideplatinum (II) nitrate at 25°:

v (liter/mole)	μ
250	102.0
500	107.6
1000	111.8
2000	116.9
4000	120.0
8000	124.0

Electrical conductivity of the amido(ethylenediamine)amideplatinum (II) nitrite at 25°:

v (liter/mole)	μ
500	117.0
1000	121.0
2000	124.3
4000	128.6

All the ethylenediamine-acetamide platinum compounds that we prepared had very similar properties and, at the same time, were considerably different in properties from the nonionic platinum acetamide compounds. Unlike the latter, the compounds prepared were so soluble that they could be isolated only from alcoholic solution. Aqueous solutions of the compounds had neutral reactions and the presence of the corresponding acid anions and complex cations could be confirmed. With potassium chloroplatinate (II) the ethylenediamine-acetamide platinum compounds formed yellow microscopic needlelike crystals, difficultly soluble in water.

We give here the analytical results for compounds obtained by the action of potassium chloroplatinate (II) on 1) the nitrate, 2) the chloride, 3) the bromide, 4) the iodide, 5) the thiocyanate, and 6) the nitrite.

Found %: 1) Pt 53.96; 54.44; Cl 12.83; 13.36.
2) Pt 53.74; 54.41; Cl 12.45; 12.88.
3) Pt 54.30; 54.36; Cl 12.53; 12.91.
4) Pt 54.50; 54.05; 54.02; Cl 13.01.
5) Pt 54.42; 54.07; Cl 12.80.
6) Pt 54.88; 54.17; Cl 12.82.

$[PtNH_2COCH_3NHCOCH_3En]_2[PtCl_4]$. Calculated %: Pt 54.11; Cl 13.15.

On the basis of the results obtained, the fact that the same compound is formed in all cases is established beyond dispute, and its composition confirms the identity of the inner spheres of all of the ethylenediamine-acetamide platinum compounds. The reaction leading to the formation of the chloroplatinate (II) can be expressed as follows:

$$2[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot En]X + K_2PtCl_4 \longrightarrow 2KX + [PtNH_2COCH_3 \cdot NHCOCH_3 \cdot En]_2[PtCl_4]$$

where X = NO_3, Cl, Br, I, CNS or NO_2.

In order finally to resolve the question whether a rearrangement occurs in the inner sphere of platinum acetamide compounds of the electrolyte type — opening of the acetamide ring and formation of an ethylenediamine ring — it is necessary to study the action of ammonia (typical of "amines" occupying one coordination position) on nonionic platinum acetamide compounds. The preparation of compounds analogous to the ethylenediamine-acetamide platinum compounds could be regarded as a proof of the absence of bond rearrangement and of the constancy of the acetamide grouping.

Reaction of Platinum Acetamide Compounds with Ammonia

It was known from previous investigations that a chloroamidoamideplatinum does not react with ammonia even after prolonged heating, and investigation was therefore directed to the most reactive compound, the nitratoamidoamideplatinum. Experiment showed that on merely being warmed with concentrated ammonia the compound dissolves, forming a yellowish solution. On evaporation of the solution to dryness and treatment of the dry residue with alcohol, it was found possible to crystallize the compound in the form of pale-yellow plates. In order to obtain homogeneous compounds, it was found necessary to carry out the evaporation of the ammoniacal solutions of the platinum acetamide compounds in presence of an excess of ammonia; otherwise, the reverse reaction occurs, and the original nitratoamidoamideplatinum separates.

Analysis gave:

Found %: Pt 50.58; 50.16.

$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot NH_3]NO_3$. Calculated %: Pt 49.92.

The electrical conductivity, determined in M. M. Yakshin's laboratory by his assistant V. M. Ezuchevskaya, characterizes the compound as a two-ion electrolyte, which is in agreement with the proposed structure.

v (liter/mole)	μ
500	91.3
1000	100.5
2000	103.6
4000	106.2
8000	110.4
16000	111.7

The properties of the compound are very close to those of the amido(ethylenediamine)amideplatinum (II) nitrate. Aqueous solutions of the compound form yellow microscopic needlelike crystals of low water-solubility with potassium chloroplatinate (II) and with sodium picrate. The analytical results for the chloroplatinate (II) are:

Found %: Pt 58.27; 59.42; Cl 14.46.

$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot NH_3]_2[PtCl_4]$. Calculated %: Pt 58.79; Cl 14.27.

The analytical results for the derivative formed by the amidoammineamideplatinum (II) nitrate with sodium picrate are:

Found %: Pt 35.00; 35.08.

$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot NH_3][C_6H_2(NO_2)_3O]$. Calculated %: Pt 35.05.

Thus, it may be considered, on the basis of the experimental results, that when ammonia reacts with the nitratoamidoamideplatinum the acidic addend is eliminated into the outer sphere and ammonia is taken up in the inner sphere with formation of a compound analogous to the amido(ethylenediamine)amideplatinum (II) nitrate. However, it was of interest to find out whether the character of the reaction is preserved also when ammonia reacts with various nonionic platinum acetamide compounds. With this aim, a study was made of the reaction of ammonia with compounds of formula

$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot X]$, where X = Cl, Br, I, CNS, or NO_2.

As a result of numerous experiments it was established that all these compounds dissolved, with varying degrees of difficulty, in concentrated ammonia with formation of pale-yellow solutions. The chloro-, thiocyanato, and nitroamidoamideplatinums were particularly difficult to dissolve. In order to dissolve the chloroamidoamideplatinum, it was necessary to treat the residues repeatedly with concentrated ammonia.

It was not found possible to isolate the ammonia-acetamide platinum compounds in the pure state, for during the evaporation of the ammoniacal solutions the reverse reactions, giving the original compounds, occur very readily. However, the compounds were characterized in the form of the derivatives formed with sodium picrate, which form microscopic yellow needles of low solubility in water.

Summarizing all the experimental results obtained in the study of the action of ethylenediamine and of ammonia on nonionic platinum acetamide compounds, we may conclude that the character of the reaction is evidently the same in all cases and consists of the elimination of acidic addends and the reception into the inner sphere of the respective amine. The mechanism of the reaction may be expressed by the following general equation:

$$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot X] + A \longrightarrow [PtNH_2COCH_3 \cdot NHCOCH_3 \cdot A]X.$$

where A = NH_3 or $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$; X = NO_3, Cl, Br, I, CNS, or NO_2.

In spite of the fact that ethylenediamine occupies only one coordination position, the ethylenediamine-acetamide platinum compounds are more stable than the ammonia-acetamide compounds, which is quite noncharacteristic for complex compounds of bivalent platinum. It is well known that in these compounds the link between ammonia and platinum is notable for its high strength.

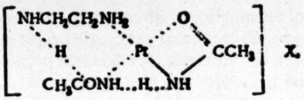
We present here the analytical results for compounds obtained by the action of sodium picrate on 1) the amidoammineamideplatinum (II) chloride, 2) the amidoammineamideplatinum (II) bromide, 3) the amidoammineamideplatinum (II) thiocyanate, 4) the amidoammineamideplatinum (II) iodide, and 5) the amidoammineamideplatinum (II) nitrite.

Found %: 1) Pt 35.15
2) Pt 35.10
3) Pt 34.75; N 14.59
4) Pt 34.81
5) Pt 35.13;

$[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot NH_3][C_6H_2(NO_2)_3O]$. Calculated %: Pt 35.05; N 15.07.

The analytical results for these compounds show that the same derivative is formed in all cases, its composition being at the same time identical with that of the picrate derivative of the amidoammineamidoplatinum (II) nitrate. Thus, there is every reason to suppose that ethylenediamine occupies only one coordination position in the platinum acetamide compounds.

The high stability of ethylenediamine-acetamide compounds of platinum and the peculiar behavior of ethylenediamine in the inner sphere of the compounds may be partially explained if the possibility is admitted of the formation of a hydrogen bond between the nitrogen of the free NH_2 group and the oxygen of the neighboring acetamide, as indicated in the following scheme:



where X = NO_3, Cl, Br, I, CNS or NO_2.

SUMMARY

1. A study has been made of the action of amines (ethylenediamine and ammonia) on nonionic platinum acetamide compounds, and it has been shown that these nonelectrolytes may be converted into compounds of the electrolyte type.

2. Ethylenediamine-acetamide and ammonia-acetamide platinum compounds have been synthesized; their structures may be represented by the following formulas: $[PtNH_2COCH_3 \cdot NHCOCH_3 \cdot A]X$, where A = En and NH_3; X = NO_3, Cl, Br, I, CNS or NO_2.

3. It has been suggested that in the ethylenediamine-acetamide platinum compounds there is a hydrogen bond between the nitrogen of the free amino group and the oxygen of the neighboring acetamide.

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REACTIONS IN SOLUTIONS OF BIVALENT PLATINUM DIAMMINES IN PRESENCE OF ULTRAVIOLET RADIATION

A.V. Babaeva and M. A. Mosyagina

A number of investigations, including ours, have shown that the absorption spectra of the majority of typical complex compounds, such as those of the platinum metals, cobalt and chromium, in the visible and ultraviolet regions consist of two or three bands. Sometimes there are no absorption bands in the visible region, so that the substance is colorless, or there may be continuous structureless absorption in the ultraviolet.

It may be regarded as established that the frequencies of the maxima of the second band, which lies in the ultraviolet region, have the effect of producing in the substance a peculiar, incomplete dissociation of the substituent and may serve as a measure of the strength of the coordinate link. For example, these frequencies bring about the decomposition of potassium trioxalatocobaltate (III), and accelerate the hydrolysis of oxalatopentamminecobalt (III) sulfate and the formation of chloropentammineplatinum (IV) chloride. The number of known photochemical reactions of this kind for complex compounds is, however, as yet small.

The classical compound – cis-dichlorodiammineplatinum, or so-called Peyrone's salt – is a compound that is fairly stable under various conditions: it is decomposed at 340°, being first converted at 290° into the trans isomer [1]; it does not undergo visible change in the light either in solution or in the crystals; in aqueous solution it is hydrated and hydrolyzed, as the rise of electrical conductivity with time shows [2], but from the acidified solution the compound may be readily recrystallized, heating being applied almost up to the boil.

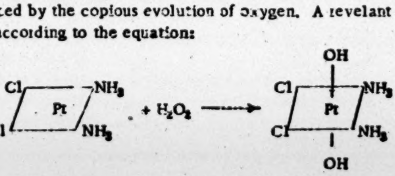
The absorption spectrum of the cis-dichlorodiammine in the visible and ultraviolet regions was studied by Liefschitz and Rosenbohm [3] in 1921. They found that the compound has only one absorption band having a maximum at 3700 A. According to our results [4], the spectrum of cis-dichlorodiammineplatinum in this region consists of three bands having maxima at 3660, 3080 and 2730 A. If the absorption of photons of ultraviolet frequency is indeed associated with distension of the bond between the central atom and the substituent, then it may be supposed that by irradiation of cis-dichlorodiammineplatinum with these frequencies in presence of water, there should be increased hydrolysis.

We set ourselves the task of investigating whether photochemical reactions do occur in a solution of this salt under the action of ultraviolet radiation, to what these reactions lead, and what frequencies are responsible for them.

EXPERIMENTAL

A saturated aqueous solution of the cis-dichlorodiammine $[(NH_3Cl)_2Pt]$ (solubility at 25°, 0.25%) was irradiated in a quartz vessel by the unfiltered radiation from a quartz mercury lamp. After 20-30 minutes, black amorphous material resembling metallic platinum began to precipitate from solution. It was quite insoluble in water and in sulfuric acid, but it dissolved in dilute hydrochloric acid not only on heating, but also in the cold. As irradiation of the original solution proceeded, its acidity increased. Also, the temperature in the reaction vessel rose, of course. Performance of the experiment in a special quartz vessel having water cooling and stirring showed that lowering of temperature encourages formation of the black precipitate.

It is known that when short-wave ultraviolet acts on water hydrogen peroxide is formed, which in our experiment, without cooling, was evidenced by the copious evolution of oxygen. A revelant hypothesis would be the oxidation of the platinum diammine according to the equation:



if the properties of the compound formed did not differ greatly from those of dichlorodihydroxodiammineplatinum, which is of a pale yellow color. The hydrolysis products from diammines are distinct also in other properties. Thus, neither hydrolysis nor oxidation with hydrogen peroxide will convert the dichlorodiammineplatinum into a black substance, and it is possible that its appearance must be ascribed to both processes acting simultaneously with participation of the energy of the ultraviolet rays.

What frequencies are responsible for this reaction and what is the substance formed? By the application of a light filter consisting of a solution of cobalt chloride in acetone, which absorbs radiation of wavelength less than 3000 A, no change could be induced in the solution, even after many hours of irradiation. Again, no black substance was formed when irradiation was effected through a solution of nickel chloride, which passes only the band of waves between 2300 and 2500 A. In short, the frequencies that are active for the compound investigated correspond to wavelengths lying between 2500 and 3000 A, i.e., those which are absorbed to give a band in the absorption spectrum having a maximum at 2730 A, and also wavelengths of less than 1900 A, which cause the photochemical formation of hydrogen peroxide from water.

In order to establish the composition of the compound formed, the black precipitate was filtered off, carefully washed with boiling water to remove traces of the original salt, and analyzed. Platinum was determined in this substance by reducing a weighed amount by evaporating down with sulfuric acid and igniting; chlorine was estimated as silver chloride in a weighed sample that was reduced by heating with sodium carbonate; and nitrogen was determined by the combustion of a micro quantity. When determining water by drying, we found that it vaporized away continuously as the temperature rose from 50 to 200° and higher. It may therefore be supposed that it was being removed also from the inner sphere.

Analytical Results

Found %: Pt 70.30, 70.74, 70.10; mean 70.38
Found %: Cl 9.25, 9.13, 9.41; mean 9.26
Found %: N 5.14, 5.21; mean 5.18

We did not succeed in determining whether the substance was an electrolyte or not, for it was impossible to determine its electrical conductivity owing to its insolubility in water.

When the black precipitate was dissolved in dilute hydrochloric acid, a cherry-red solution was obtained, from which, when heated on a water bath for thirty minutes, crystals of ammonium chloroplatinate (IV) separated. Ammonium trichloroammineplatinate (II) was extracted from the solution that had been concentrated on the water bath. The compositions of these compounds were confirmed by analysis for platinum.

Found %: Pt 44.01, 44.25
$(NH_4)_2PtCl_6$ Calculated %: Pt 43.94

Found %: Pt 55.56
$NH_4[NH_3Cl_3Pt]$. Calculated %: Pt 55.05

From the hydrochloric acid solution the monoammine was isolated also by means of a solution of $[(NH_3)_4Pt]Cl_2$ in the form of the tetrammine salt $[(NH_3)_4Pt][NH_3Cl_3Pt]_2$, which formed light brown scalelike crystals.

Found %: Pt 64.75, 64.60, 65.12.
$[(NH_3)_4Pt][NH_3Cl_3Pt]_2$. Calc.%: Pt 64.71

The investigated compound, when oxidized with chlorine in aqueous suspension, became brown. From a solution of the brown substance in dilute hydrochloric acid ammonium chloride caused the precipitation of chloroplatinate (IV), and from the mother liquor yellow prisms of $NH_4[NH_3Cl_5Pt]H_2O$ crystallized out, the platinum content being 48.56%, and the water content 3.66% (calculated from the formula: platinum 47.96%, water 4.23%).

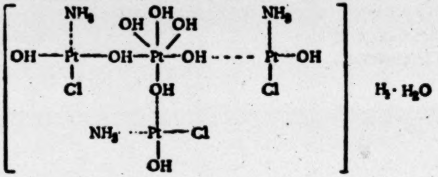
It follows from these experiments that both bi- and quadri-valent platinum enter into the composition of the compound formed by the action of ultraviolet radiation on Peyrone's salt. In order to establish the bi-quadri ratio, the substance was oxidized quantitatively with potassium permanganate. For this purpose, diluted (1:2) hydrochloric acid was added dropwise to a weighed amount of the compound, the reaction mixture being heated on a water bath. Then, as usual, sulfuric acid was added and the solution was titrated potentiometrically with permanganate.

Found %: Pt 51.87, 53.63; mean 52.70

As the platinum content of the investigated substance was 70.38%, it follows that the ratio of Pt^{IV} to Pt^{II} was about 1:3, and the ratio Pt:Cl:N was about 4:3:3.

From a comparative examination of the analytical results and the properties of the product of the irradiation of cis-dichlorodiammineplatinum the conclusion may be drawn that the product is evidently a polynuclear compound of bi- and quadri-valent platinum containing water of crystallization, during the estimation of which by drying, a portion of water is removed also from the inner sphere, where it is fixed in the form of hydroxyl groups attached to the platinum atom. There is nothing surprising in this behavior of hydroxyl groups, for it is characteristic of the radical of the hexahydroxo acid $[Pt(OH)_6]$, which is present in this compound. Evidently, the bivalent platinum atoms are linked with the quadrivalent platinum by hydroxyl bridges, which are ruptured by reaction with hydrochloric acid.

This compound must probably be assigned the following structure:



A compound of this structure should contain 70.27% platinum, 9.26% chlorine, 3.78% nitrogen; analysis gave 70.38% platinum, 9.37% chlorine, 5.21% nitrogen.

Irradiation by ultraviolet rays of the monoammine $K[NH_3Cl_3Pt]$ also led to a compound of similar composition.

Found %: Pt 70.30, 70.17, Cl 8.31

In a solution of trans-dichlorodiammineplatinum, which is characterized, according to our results [4], by an absorption spectrum having absorption maxima at 3760, 3170 and 2730 A, the action of ultraviolet radiation also leads to reaction, leading to formation of a precipitate of brown color. However, the rate of this reaction is so low that a two-month irradiation was necessary in order that sufficient substance could be accumulated for investigation purposes.

This, like the previous substance, dissolves in dilute hydrochloric acid, from which, on addition of ammonium chloride, ammonium chloroplatinate (IV) is precipitated; addition of a solution of tetrammineplatinum (II) chloride $[(NH_3)_4Pt]Cl_2$ leads to precipitation of a mixture of Magnus's salt – $[(NH_3)_4Pt][PtCl_4]$, $[(NH_3)_4Pt][NH_3Cl_3Pt]_2$ and $[(NH_3)_4Cl_2Pt]Cl_2$, which are formed as a result of the following reactions:

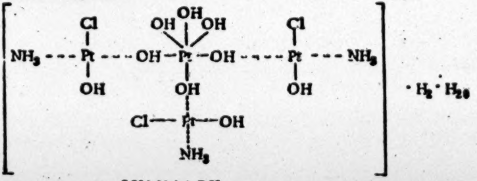
1. $H_2PtCl_6 + [(NH_3)_4Pt]Cl_2 \rightarrow [(NH_3)_4Pt][PtCl_6] + [(NH_3)_4Cl_2Pt]Cl_2 + HCl$;

2. $[NH_3Cl_3Pt]^- + [(NH_2)_4Pt]^{++} \rightarrow [(NH_3)_4Pt][NH_3Cl_3Pt]_2$.

Analytical results for the brown compound:

Found %: Pt 70.24, 70.20, 70.16
Found %: Cl 8.70, 8.89
Found %: N 4.16, 4.15

Titration with potassium permanganate gave about 1:3; for the ratio $Pt^{IV}:Pt^{II}$. We consider it possible to assign the following structure, analogous to that for the compound obtained from cis-dichlorodiammineplatinum to the substance derived from the trans compound:



SUMMARY

1. It has been shown that in solutions of cis- and trans-dichlorodiammineplatinums the presence of ultraviolet radiation leads to the formation of polynuclear compounds of bi- and quadri-valent platinum having hydroxyl bridges.

2. The active frequencies correspond to the absorption band of these compounds having a maximum at 2730 A.

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COMPLEX COMPOUNDS OF PLATINUM WITH DIALLYLAMINE

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The first reference to complex compounds of platinum with unsaturated molecules occurred in 1829. By treating platinous chloride with alcohol and then with potassium chloride or ammonium chloride, Zeise obtained crystalline salts, the chemical composition of which he expressed by the formula $Me[PtC_2H_4Cl_3] \cdot H_2O$. At that time a number of chemists doubted the existence of these compounds, which were soon forogtten, but the existence of these substances, which had been described by Zeise in 1829, received some confirmation in 1861, when it was found that the gas evolved when such compounds are heated is ethylene C_2H_4.

In 1861 Birnbaum obtained the salt $Me[PtC_2H_4Cl_3]H_2O$ by direct synthesis from ethylene and platinous chloride, and later a number of investigators more or less successfully examined the question of preparing analagous compounds. The investigations of Jorgensen must probably be considered as the most important of these studies; they again confirmed the correctness of Zeise's formulas and established that analogous properties are possessed by the salts $Me[PtC_2H_4Cl_3]$ and the salts $Me[PtAX_3]$, where A is an amine and X is Cl or Br, etc.

These analogies, when the peculiar features of ethylene compounds were neglected, placed the compounds in the general series of amines. Numerous researches by a number of other investigators on the compounds of platinum with ethylene homologs and unsaturated aromatic compounds gave reason for the postulation of the existence of a special class comprising compounds of this type. However, the absence in these investigations of systematic treatment and definite aim, and sometimes also inadequate care in carrying out the experiments, did not permit the place of these compounds in the general array of complex compounds to be established.

The first complete and systematic investigation of the complex compounds of platinum with unsaturated molecules was carried out in the Kurnakov Institute of General and Inorganic Chemistry by Chernyaev and Gelman [1]. Later, in an extensive investigation, Gelman [2] synthesized and investigated compounds of platinum with ethylene and some of its homologs, with compounds of the butadiene type, with diallyl, with nitric oxide, with carbon monoxide, etc. It was then found that substituents having double bonds had increased trans activity. It was established also that, in compounds having two double bonds, each individual bond can participate in complex formation, but the molecule of the unsaturated compound does not form a ring with the central atom. It was shown in this work that all the investigated unsaturated molecules form complex compounds only with bivalent platinum, that it is impossible to prepare compounds containing two or more unsaturated molecules in the inner sphere, and that the unsaturated molecules cannot form closed rings with the platinum.

The experiments carried out earlier by Rubinshtein [3,4] on the complex compounds of platinum with amines such as α- and β-aminopyridines and aminohalopyridines again did not result in the preparation of compounds having an inner-sphere ring. Each amine occupied one coordination position.

The present investigation is devoted to complex compounds of platinum with diallylamine. The study of complex compounds of this type is of significance in connection with the question of ring formation in complex compounds. Diallylamine is of special interest as a substituent in the present case, for it is unsaturated. Hitherto, in the complex compounds of platinum, no cases of the ring closure of unsaturated compounds have been observed. In the case of diallylamine it might be expected that complex compounds of cyclic structure could be formed, since here both the nitrogen of the NH group and the double bonds can participate in complex formation.

Our investigations show that under defined conditions diallylamine forms stable complex compounds of cyclic structure with platinum. The properties of these compounds have been studied, and inner-sphere substitution reactions and the conditions required for the making and breaking of the diallylamine ring have been studied. It has been found in the course of the work that diallylamine gives cyclic complex compounds only by reaction with ammonium chloroplatinate (II) and only in neutral medium. In acid medium, and also when potassium chloroplatinate (II) is used, the reaction with diallylamine has a completely different course.

EXPERIMENTAL

I. Study of the Reaction of Diallylamine with Ammonium Chloroplatinate (II)

The calculated amount of diallylamine, as required by the reaction

$$(NH_4)_2PtCl_4 + [CH_2{=}CHCH_2]_2NH \rightarrow [(CH_2{=}CHCH_2)_2NHCl_2Pt] + 2NH_4Cl\ .$$

(one molecule of diallylamine to one molecule of chloroplatinate (II) was added in the cold to a saturated neutral solution of ammonium chloroplatinate (II) (in formulas, diallylamine $(CH_2{=}CHCH_2)_2$ NH will in future be denoted by D). Dichloro(diallylamine)platinum DCl_2Pt began to separate as a dark yellow precipitate as soon as the solutions were mixed. The salt was filtered off and dried in a desiccator at ordinary temperature, for all diallylamine compounds decompose at elevated temperatures. When the dark yellow salt had been filtered off, a second, light yellow salt separated. It was established by crystal-optical analysis that both salts were free from impurities and had refractive indices of 1.68 (dark yellow) and 1.72 (light yellow).

Chemical analysis showed that both salts had the same contents of platinum, chlorine and nitrogen. Whereas the dark yellow salt gave Pt 53.57, 53.67%; Cl 19.90, 19.87%; N 5.04%; the light yellow salt that separated in the second stage of the reaction between diallylamine and ammonium chloroplatinate (II) gave Pt 53.51, 53.30%; Cl 19.29%; N 4.18, 4.57%.

The calculated values for a compound of formula DCl_2Pt are Pt 53.78%; Cl 19.52%; N 3.85%. In spite of their identity in percentage composition, the two salts are distinct in color and solubility (the dark yellow salt is not readily wetted by water and is insoluble; the solubility of the light yellow salt is 0.040 g per 100 g of solution), and also in refractive index (dark yellow 1.68; light yellow 1.72). By analogy with the reaction of ammonium chloroplatinate (II) with ammonia, as a result of which cis-dichlorodiammineplatinum $(NH_3Cl)_2Pt$ and its dimer $[4NH_3Pt][PtCl_4]$, are formed, we supposed that in this case also a monomer, the dark yellow salt DCl_2Pt, and a dimer, the light yellow salt $[D_2Pt][PtCl_4]$ are formed. This supposition was confirmed by the formation of the salt $[D_2Pt][PtCl_4]$ on addition of chloroplatinate (II) to a solution obtained by the action of an excess of diallylamine on DCl_2Pt. In order to prove the identity of the two salts we determined their solubilities: the respective values were 0.040 and 0.035 g per 100 g of solution.

Thus, by the action of diallylamine on ammonium chloroplatinate (II) in neutral solution, two compounds DCl_2Pt and $[D_2Pt][PtCl_4]$ were obtained; in these diallylamine occupies two coordination positions and consequently forms a ring.

Reactions of dichloro(diallylamine)platinum with ammonia and with pyridine.

A study of the reactions of dichloro(diallylamine)platinum DCl_2Pt with ammonia and with pyridine yielded confirmatory evidence of the existence and stability of the diallylamine ring. When DCl_2Pt was warmed carefully with ammonia or pyridine, the salt dissolved with formation of a reddish-brown (for ammonia) or brownish-yellow (for pyridine) solution. Evaporation of the solution yielded a dark brown or orange-red salt (respectively). If we suppose that the reaction of diallyl amine with an amine proceeds according to the equation

$$DCl_2Pt + 2\ A = D2\ APtCl_2,$$

where A = NH_3 or Py, then we have for the salts obtained:

$D(NH_3)_2PtCl_2$.	Found %:	Pt 49.01, 48.19;	Cl 18.17, 18.40;	N 10.49, 10.20
	Calculated %:	Pt 49.14	Cl 17.84	N 10.57
DPy_2PtCl_2.	Found %:	Pt 37.35,	Cl 14.10,	N 8.74, 8.62
	Calculated %:	Pt 37.43	Cl 13.59	N 8.05

The two mixed amine-diallylamine compounds were obtained also by neutralization of solutions of $D(NH_3)_2PtCl_2$ and DPy_2PtCl_2 with hydrochloric acid. Also, they were isolated and characterized in the form of a chloroplatinate (II) $[DA_2Pt][PtCl_4]$.

Reaction of dichloro(diallylamine)platinum with thiourea.

When a saturated solution of thiourea (it is indifferent whether the calculated amount or an excess of thiourea is used) reacted with dichloro (diallylamine) platinum DCl_2Pt, the salt dissolved and a dark red-brown solution was formed. When this solution was evaporated, a dark-colored precipitate separated and was washed carefully with alcohol to free it from excess of thiourea. Chemical analysis of the dry salt gave Pt 37.60%, 37.73%; N 13.83%. If we suppose that the reaction between thiourea and DCl_2Pt proceeds according to the equation:

$$DCl_2Pt + 2Thio = DThio_2PtCl_2$$

calculation for $DThio_2 \cdot PtCl_2$ gives Pt 37.88%, N 13.59%. Thus, even under the action of thiourea the diallylamine ring is not destroyed.

Action of hydrochloric acid on DCl_2Pt and the opening of the diallylamine ring.

In the compounds that we have just discussed, diallylamine occupies two coordination positions. It was of considerable interest to find conditions for the preparation of compounds in which diallylamine would occupy only one coordination position. With this purpose a study was made of the reaction of hydrochloric acid on dichloro (diallylamine)platinum DCl_2Pt and on the mixed ammonia-diallylamine tetrammine $D(NH_3)_3PtCl_2$. It was found that hydrochloric acid (1:2) applied at the boil caused the opening of the diallylamine ring of DCl_2Pt, yielding a compound of composition $HDCl_3Pt$, in which the diallylamine is contained in a complex anion. Chemical analysis of the compound obtained gave the following results:

Found %: Pt 48.98, 49.52, 48.78, 49.47; Cl 27.23, 26.75; N 3.51, 3.76
$HDCl_3Pt$. Calculated %: Pt 48.83; Cl 26.66, N 3.50

By the action of the tetrammine chloride $[(NH_3)_4Pt]Cl_2$ on a hydrochloric acid solution of DCl_2Pt, the salt $[(NH_3)_4Pt][DCl_3Pt]_2$ was precipitated; its composition was established by analysis:

Found %: Pt 55.73, 55.15; N 7.44
$[(NH_3)_4Pt][DCl_3Pt]_2$ Calculated %: Pt 55.21, N 7.92

The presence in this salt of the cation $[(NH_3)_4Pt]^{++}$ was readily revealed by treatment at the boil with chloroplatinate (II). The characteristic green salt $[NH_3)_4Pt]PtCl$ was then formed. Thus, boiling with hydrochloric acid (1:2) leads to opening of the diallylamine ring.

The reactions of the compound $HDCl_3Pt$ (monoammine I) with ammonia, thiourea and caustic alkali were studied.

a) Reaction with ammonia.

When the compound $HDCl_3Pt$ was carefully warmed with ammonia, it dissolved, and when the solution obtained was evaporated a dark brown precipitate separated. The precipitate was not homogeneous, and its composition could therefore not be determined. Treatment with water caused part of the precipitate to dissolve, giving a solution that gave a precipitate with ammonium chloroplatinate (II). We considered that the reaction between ammonia and monoammine I, $HDCl_3Pt$, proceeds as follows:

$$HDCl_3Pt + 4NH_3 \rightarrow D(NH_3)_3PtCl_2 + NH_4Cl$$

and further:

$$D(NH_3)_3PtCl_2 + (NH_4)_2PtCl_4 = [D(NH_3)_3Pt][PtCl_4] + 2NH_4Cl.$$

Analysis confirmed our supposition:

Found %: Pt 57.12, 57.24; N 7.89
$[D(NH_3)_3Pt][PtCl_4]$. Calculated %: Pt 57.67, N 8.23

By the action of ammonia on monoammine I, $HDCl_3Pt$, a mixed tetrammine is obtained in which diallylamine again occupies one coordination position.

b) Reaction with thiourea.

A saturated solution of thiourea partly dissolved the mono ammine $HDCl_3Pt$ even in the cold, but for complete dissolution it was necessary to heat to the boil. When dissolution was complete, the solution was allowed to evaporate freely. The precipitate that separated was carefully washed free from excess thiourea by means of alcohol; it was lemon yellow. The reaction proceeded according to the equation:

$$HDCl_3Pt + 4Thio \rightarrow 4ThioPtCl_2 + D \cdot HCl.$$

Found %: Pt 34.16, 33.69; Cl 12.90, N 18.68
$4Thio_4PtCl_2$. Calculated %: Pt 34.23, Cl 12.43, N 19.03

The salt is of good solubility in water, and its aqueous solution, acidified with nitric acid, gives an immediate precipitate of silver chloride with silver nitrate. Thus, in compounds in which diallylamine does not form a ring, treatment with urea leads to complete elimination of diallylamine from the inner sphere.

c) Reaction with caustic alkali and cyclization.

If the dry salt $HDCl_3Pt$ is treated with 5% NaOH and the mixture is heated on a water bath, cyclization of the diallylamine group occurs with formation of dichloro(diallylamine) platinum DCl_2Pt. The performance of this reaction gives some difficulty. If the reaction mixture is heated until the monoammine has completely reacted, then part of thedichloro(diallylamine)platinum is converted into a hydroxo salt; otherwise, part of the monoammine remains unchanged and affects the analytical results:

Found %: Pt 52.89; Cl 21.08

DCl_2Pt. Calculated %: Pt 53.73; Cl 19.52

In the original monoammine $HDCl_3Pt$ %: Pt 48.83; Cl 26.61

Such are the properties of the compound obtained by the reaction between diallylamine and ammonium chloroplatinate (II) in neutral medium.

Action of hydrochloric acid on the mixed ammonia-diallylamine tetrammine $D(NH_3)_2PtCl_2$.

In view of the results of the investigations of the reaction of hydrochloric acid with dichloro(diallylamine) platinum, leading to the opening of the diallylamine ring, it was of interest to investigate the action of HCl on ammonia-diallylamine compounds, in particular $D(NH_3)_2PtCl_2$. Our experiments gave positive results, and it was established that, when hydrochloric acid reacts with the tetrammine $D(NH_3)_2PtCl_2$, one or two ammonia molecules, depending on the duration of heating only, are split off without disturbance of the ring. The resulting compounds are of the triammine and diammine series respectively: $DNH_3ClPtCl$ and DCl_2Pt. The respective reactions may be represented by the following equations:

$$D(NH_3)_2PtCl_2 \xrightarrow{HCl} DNH_3ClPtCl + NH_4Cl; \qquad (1)$$

$$D(NH_3)_2PtCl_2 \xrightarrow{2HCl} DCl_2Pt + 2NH_4Cl. \qquad (2)$$

The analytical results for the compound obtained by the first of these reactions are:

Found %: Pt 51.01, 50.86, 51.97; N 6.60, 7.41

$DNH_3ClPtCl$. Calculated %: Pt 51.33 N 7.36

and for the compound obtained by the second reaction:

Found %: Pt 53.77, 53.66, 53.50; Cl 20.16, 20.44

DCl_2Pt. Calculated %: Pt 53.73 Cl 19.51

The two reactions are carried out by careful heating of the terammmine $D(NH_3)_2PtCl_2$ with hydrochloric acid. The first ammonia molecule splits off particularly readily, possibly because this ammonia molecule is trans to the double bond.

II. Reaction of Diallylamine with Ammonium or Potassium Chloroplatinate (II) in Acid Medium and the Preparation of Monoammine II $HDCl_3Pt$.

The action of diallylamine on potassium chloroplatinate (II) in neutral medium does not lead to the isolation of any definite compounds. When diallylamine was added to an acidified solution of ammonium chloroplatinate (II) [0.5 g $(NH_4)_2PtCl_4$ + 4 ml H_2O + 2 ml conc. HCl], a bright yellow salt formed after about a day. Crystal-optical analysis indicated that the salt was homogeneous.

Found %: Pt 48.48; Cl 26.53; N 4.14

Ratio Cl/Pt = 3, N/Pt = 1.

The reaction between diallylamine and potassium chloroplatinate (II) in acid medium went in a completely similar fashion. The precipitate was bright yellow and contained 48.83% Pt, 26.77% Cl and 3.99% N. Again, Cl/Pt = 3, N/Pt = 1.

By a comparison of these results with the results of the analysis of the salt $HDCl_3Pt$, obtained by splitting dichloro(diallylamine)platinum with hydrochloric acid, we concluded that in this case a monoammine $HDCl_3Pt$ was formed; this we indicated by the figure II, having in view the method by which it was prepared. We were confirmed in this view also by a comparison of the refractive indices of the two salts. Thus, for monoammine $HDCl_3Pt$ (I): Ng 1.765; Np 1.680; and for monoammine $HDCl_3Pt$ (II): Ng 1.767; Np 1.680.

Monoammine II gave the same inner-sphere substitution reactions as monoammine I. For comparison we give the results of the corresponding experiments: a) the reaction with ammonia proceeded in completely analogous fashion, the salt obtained being isolated as chloroplatinate (II), in which was found Pt 57.77% and N 8.14%; b) with thiourea under the same conditions a lemon-yellow salt, containing 34.16% Pt, was formed; c) with a 5% solution of caustic soda a dark yellow salt, containing Pt 53.38% Cl 18.68% was obtained.

Hence it may be concluded that both in the splitting of dichloro(diallylamine)platinum DCl_2Pt with hydrochloric acid and in the reaction between diallylamine and ammonium or potassium chloroplatinate (II) in acid medium, the same compound, the monoammine $HDCl_3Pt$, is formed.

The experimentally observed fact that ammonium chloroplatinate (II) and potassium chloroplatinate (II) react differently with diallylamine in acid medium deserves particular attention.

SUMMARY

1. The action of diallylamine on ammonium chloroplatinate (II) in neutral medium has been studied, and it has been shown that the monomer DCl_2Pt and the dimer $[D_2Pt][PtCl_4]$ are formed. In these compounds diallylamine occupies two coordination positions and forms a ring.

2. The view is expressed that diallylamine, in forming a ring with the platinum, unites through the nitrogen of the NH group and the double bond.

3. It has been shown that thiourea reacts with DCl_2Pt with formation of $DThio_2PtCl_2$, so confirming the stability of the diallylamine ring. The preparation of mixed ammonia-diallylamine compounds is also an indication of the stability of the diallylamine ring.

4. The action of concentrated HCl on DCl_2Pt has been studied, and it has been shown that the ring may be opened with formation of the compound $HDCl_3Pt$, in which diallylamine occupies one coordination position. A study of the reaction of this compound with thiourea has shown that diallylamine, when occupying one coordination position, is readily eliminated from the inner sphere with formation of the compound $Thio_4PtCl_2$.

5. The reaction of diallylamine with chloroplatinates (II) in acid medium has been studied. It has been shown that a compound $HDCl_3Pt$ is obtained which is identical with the compound $HDCl_3Pt$ obtained by boiling DCl_2Pt with concentrated HCl.

6. The reaction conditions have been found under which the re-closure of the ring occurs in the compound $HDCl_3Pt$.

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STRUCTURE OF THE COMPLEX ION $[Co(NO_2)_4(NH_3)_2]'$

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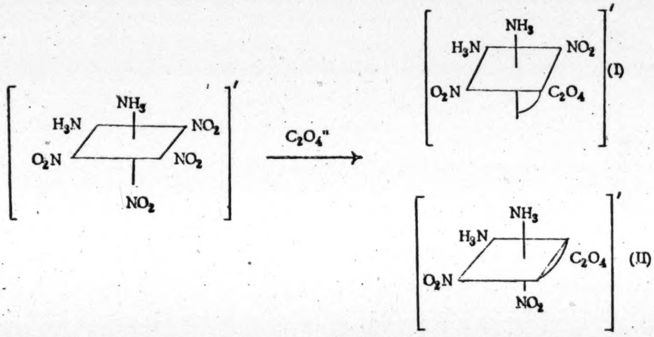
According to coordination theory the ion $[Co(NO_2)_4(NH_3)_2]'$ should exist in two forms, cis and trans. However, only one isomer is known. There is the contradictory evidence concerning the structure of this ion. The following facts support the cis configuration:

1) The absorption spectrum of $NH_4[Co(NO_2)_4(NH_3)_2]$ in the visible and ultraviolet regions consists of three characteristic bands. The same sort of absorption, with the same number and position of bands, is shown by trans-dinitrotetramminecobalt (III) chloride, whereas for the cis-dinitrotetrammine chloride the third band is absent. The third band disappears also for the compound $NH_4[Co(NH_3)_2C_2O_4(NO_2)_2]$, which is obtained from $NH_4[Co(NO_2)_4(NH_3)_2]$ by reaction with oxalic acid. A comparison of the spectra of these four compounds [1] has led to the conclusion that the presence of the third band is caused by the coordinate linkage $NO_2-Co-NO_2$, and that in the compound $NH_4[Co(NO_2)_4(NH_3)_2]$ only two NO_2 groups are in a trans position.

2) By the action of oxalic acid, two isomers of the compound $[Co(NH_3)_2C_2O_4(NO_2)_2]_2Ba$ have been obtained [2], one of which is resolved by strychnine into enantiomorphs. This fact is readily explained by a cis structure in the complex:



The isomer II, having as asymmetric structure, is capbale of being resolved into enantiomorphs.

The following facts support the trans confiruration:

1) Reaction with ethylenediamine [3] gave $[Co(NO_2)_3(NH_3)En]$ as sole product. If the structure had been cis, the ethylenediamine would have eliminated the two adjacent NH_3 molecules. 2) In spite of a number of attempts, it was not found possible to resolve dioxalato-substituted tetranitrodiamminecobaltate (III) into enantiomorphs [3], thus indicating a symmetrical structure for the dioxalato compound: an asymmetric dioxalato compound should have been obtained if the NH_3 groups had cis relationship in the tetranitrodiammine. 3) An investigation [4] and comparison of the absorption spectra of a number of nitro ammines of tervalent cobalt in the region 320-350 mμ (second spectral band) led to the conclusion, when the degrees of absorption and the position of the absorption maxima were taken into consideration, that the ion $[Co(NO_2)_4(NH_3)_2]'$ contains two $NO_2-Co-NO_2$ bonds. 4) X-Ray structure investigation of $Ag[Co(NO_2)_4(NH_3)_2]$ [5] has established the trans configuration in the crystals of this compound.

The contradictory data concerning the structure of the ion $[Co(NO_2)_4(NH_3)_2]'$ led Chernyaev in 1927 to suggest [6] that some investigators were working with one isomer, and some with the other. However, this suggestion is disproved by the constancy of the goniometric constants cited by the authors of both groups of investigations.

Only the earliest investigations (through 1923) have been critically reviewed in the literature, and for some reason or other the last two investigations pointing to the trans positions of the NH_3 groups in the complex $[Co(NO_2)_4(NH_3)_2]'$ have passed unnoticed. Analysis of the earlier results led to a preference for the cis hypothesis, for the proof of the trans structure was acknowledged to be unconvincing. Thus, the course of the reaction with ethylenediamine is explained by Grinberg [7] by the mobility of the adjacent groups NH_3 and NO_2 in the complex of the cis isomer, and it was possible to explain the lack of success in resolving the dioxalato derivative by imperfect technique [8]. This point of view, i.e., acceptance of the proof for the cis structure as satisfactory, is maintained by the authors of several chemical reference books [8] and also by the authors of recently published monographs on the structure of complex compounds [7,9].

Thus, the view acknowledging the cis configuration for tetranitrodiamminecobaltate [III] has become accepted in the chemistry of complex compounds. The appearance of further work, spectral and, particularly, X-ray [5], compels us, however, to treat this conclusion critically and to analyze the proof of the cis structure for the complex $[Co(NO_2)_4(NH_3)_2]'$. It is sufficient to consider the fact that these assertions are based on the properties of compounds of the type $Me[Co(NO_2)_2(NH_3)_2C_2O_4]$, which are prepared from the tetranitrodiammine by reaction with oxalic acid. It is assumed that inner-sphere rearrangement during the reaction does not occur, although this supposition has never been verified for compounds of this type. The opposite hypothesis of isomerization of the complex under the action of oxalic acid makes the existence of the contradictory evidence concerning the structure of the complex ion $[Co(NO_2)_4(NH_3)_2]'$ understandable.

The soundness of this hypothesis depends on the conclusiveness of the facts cited in favor of a trans structure for the complex. The nonconclusiveness of the first two proofs has been reviewed above. As regards the spectral work of 1937 [4], it has the defect of resting on the comparative method, which permits conclusions to be drawn only on the basis of analogies in absorption spectra. The most trustworthy method of investigation in the given case appears to be the X-ray-structure method. An X-ray investigation of $Ag[Co(NO_2)_4(NH_3)_2]$ [5] has shown that the complex has a trans structure, but analysis of this work shows that the author took the presupposed trans model of the complex as basis and did not examine all the possible arrangements of atoms in the crystal lattice. Hence, in order to determine the structure of the complex $[Co(NO_2)_4(NH_3)_2]'$, we have undertaken a verification of the structural type of $Ag[Co(NO_2)_4(NH_3)_2]$ and have determined the structural type of $K[Co(NO_2)_4(NH_3)_2]$.

EXPERIMENTAL

I. Repeat Determination of the Structural Type of $Ag[Co(NO_2)_4(NH_3)_2]$

The compound $Ag[Co(NO_2)_4(NH_3)_2]$ was prepared from the analogous ammonium salt by double decomposition. It was found possible by crystallization to obtain only very fine crystals of octahedral or tabular habit (according to the rate at which the supersaturated solution was cooled). The goniometric and optical properties of the crystals were identical. Optical constants: $Nm > 1.782$; $Np = 1.665$; indicatrix negative. Symmetry of external form from goniometric measurements: 4/mmm; goniometric $c/a = 1.495$.

TABLE

Distance	Wells' results	Our results
Co–N(NH$_3$)	2.30	1.95 ± 0.03
Co–N(NO$_2$)	1.92	1.96 ± 0.03
N–O	1.25	1.25 ± 0.05
O–O	2.08	2.15 ± 0.05

By the aid of X-ray photographs and by harmonic analysis of the reflection intensities, the structural type assigned by Wells was confirmed. The structure may be described as the closest possible packing of the complex ions $[Co(NO_2)_4(NH_3)_2]'$, the Ag^+ ions being disposed in the empty octahedral spaces of the structure. The compound is the trans isomer. The fundamental X-ray constants are $a = 6.95$; $c = 10.45$; $c/a_{(X\text{-}ray)} = 1.490$. Fedorov symmetry group $D_{4h} = P4/nnc$. The five structural parameters: $u(z_{NH_3}) = 0.187$; $v(x_N) = 0.200$; $x_0 = 0.305$; $y_0 = 0.225$; $z_0 = 0.096$. The interatomic distances in the complex are given in the table.

II. Determination of the Structural Type of $K[Co(NO_2)_4(NH_3)_2]$

The compound $NH_4[Co(NO_2)_4(NH_3)_2]$ was prepared by the usual method, which is based on the reaction:

$$2CoCl_2 + 8NH_4NO_2 + 2NH_3 + \tfrac{1}{2} O_2 = 4NH_4Cl + H_2O + 2NH_4[Co(NO_2)_4(NH_3)_2].$$

The analogous potassium and thallium salts were obtained by double decomposition. Crystals of the three salts were measured on the goniometer. Refractive indices were determined by the immersion method in white light and also, for $K[Co(NO_2)_4(NH_3)_2]$, in monochromatic light. The crystals were found to have a symmetry of 222, whereas they are described in the literature as rhombodipyramidal (mmm). The refractive indices of $K[Co(NO_2)_4(NH_3)_2]$ in white light are $Ng = 1.752$; $Nm = 1.716$; $Np = 1.708$. The experimentally found refractive indices are compared by the method proposed in 1948 by Boky [10] with calculated values and it was found that they corresponded most closely with the values calculated on the assumption of the trans configuration for the complex. Peculiarities in the orientation of the optical indicatrix in $K[Co(NO_2)_4(NH_3)_2]$ and $Ag[Co(NO_2)_4(NH_3)_2]$ crystals led to a limitation of the possible positions of the complex in the lattice.

	X-ray Constants			
	a	b	c	v
$K[Co(NO_2)_4(NH_3)_2]$	11.27	12.76	6.72	964
$NH_4[Co(NO_2)_4(NH_3)_2]$	11.43	12.92	6.73	986

Fedorov symmetry group $D_2^4 = P2_12_12_1$

By a combination of harmonic analysis of X-ray interference intensities with geometric analysis by the aid of space models the structure variant corresponding most closely to the experimental results was found. In the structure so found the NH_3 groups are trans to one another.

The structure of $K[Co(NO_2)_4(NH_3)_2]$ is close to that of $Ag[Co(NO_2)_4(NH_3)_2]$. Replacement of Ag atoms in the latter compound by potassium atoms leads to the following distortions in the lattice of $Ag[Co(NO_2)_4(NH_3)_2]$: 1) increase in the parameter "a" from 10.4 to 11.2; disturbance of the coplanarity of the layers; 3) conversion of the octahedral coordination polyhedron of the Ag atom into a trigonal prism around the K atom. The peculiarities of the structure explain some of the physical properties of the crystals: the orientation of the optical indicatrix and the perfect [110] prism cleavage of the crystals.

The direct X-ray method of analysis shows, in contradiction to the chemical methods, that the complex ion $[Co(NO_2)_4(NH_3)_2]^-$ has the trans configuration. This fact shows that in those cases in which the probability of inner-sphere rearrangements is great (in the compounds of elements having complex-forming properties poorer than those of platinum) it is essential when determining structure to have recourse to physical methods, particularly X-ray structural analysis.

SUMMARY

1. For the first time, the crystal-optical method has been used for determining the structure of a complex ion; it led to the conclusion that the ion $[Co(NO_2)_4(NH_3)_2]^-$ has the trans configuration.

2. The trans configuration of the complex ion has been proved also by direct X-ray structural analysis of the compounds $Ag[Co(NO_2)_4(NH_3)_2]$ and $K[Co(NO_2)_4(NH_3)_2]'$, which belong to different structural types.

3. The fact that the NH_3 groups are in cis positions in the ion $[Co(NO_2)_2C_2O_4(NH_3)_2]^-$ [2] proves, when our results concerning the trans structure of the tetranitrodiamminecobaltate (III) from which it is derived are taken into account, that, under the influence of the oxalate ion in solution, a rearrangement of substituents of the complex occurs. The probability of such rearrangements for cobalt complex compounds (and other atoms having not very powerful complex-forming properties) is evidently greater than is usually supposed. Consequently, the role and significance of direct physical methods for the determination of the structures of complex compounds is increased.

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HYDRATION OF IONS IN AQUEOUS SOLUTION

O. Ya. Samoilov

The determining significance of the interaction between solute and solvent for the properties of solutions was first pointed out by Mendeleev. Mendeleev was also the first to point out the necessity for the development of a theory of the liquid state as a prerequisite of the study of solutions [1]. In the present paper the phenomenon of ion hydration in aqueous solutions is examined in its relation to existing data concerning the nature of the thermal agitation of the particles of the liquid and also in its relation to concepts concerning the structure of dilute aqueous solutions of electrolytes, based mainly on the study of the coordination numbers of ions in aqueous solutions.

In numerous investigations devoted to the question of ion hydration, the authors try to determine the number of water molecules bound to ions in solution — the so-called hydration numbers. However, the hydration numbers determined for particular ions from various properties of the solutions generally vary considerably among themselves. Ulich [2] and Darmois [3] in examining the phenomenon of ion hydration employ Stokes' law. Although the possibility of applying this law to the case of ionic movements in solution is subject to some doubt, it must nevertheless be considered that it permits an evaluation of quantities that are essential for the understanding of hydration. We shall examine the movement of an ion in an infinitely dilute aqueous solution. If Stokes' law is applicable

$$U\eta r = \text{const}, \qquad (1)$$

where U is the electrochemical mobility of the ion in infinitely dilute solution at a certain temperature; η is the viscosity of the medium at the same temperature; and $\underline{r}$ is the ionic radius. If the viscosity is measured in poises and ionic radii in Angstroms, then the numerical value of the constant is 0.820 Z, where Z is the ionic charge. The constant is independent of temperature.

If in Equation 1 we substitute the values of ionic mobility found experimentally and take the viscosity of the medium to be that of pure water, then the equation gives values for the ionic radii (r_s) which are in general different from the crystallographic values (r_c). These radii are called Stokes radii. A collection of data on the Stokes radii of a large number of ions is given by Darmois [3].

If for any ion $r_s > r_c$, it is assumed that the ion is hydrated in aqueous solution; if $r_s < r_c$, it is assumed that the ion is not hydrated. Darmois and Ulich determined hydration numbers from the excess of the Stokes ionic volumes over the crystallographic volumes. As is known, it is usual to explain the increase in a series such as Li^+, Na^+, K^+, Rb^+, Cs^+, in the electrochemical mobility of ions by the diminution in the series in Stokes radius. It appears, however, that such an approach does not correspond to the nature of the phenomenon of ion hydration in solutions.

Darmois [3] drew attention to the fact that temperature coefficients for the mobilities of hydrating ions (e.g. at 18°) are greater, and those of nonhydrating ions are less, than the absolute value of the temperature coefficient of the viscosity of water at the same temperature. However, it would appear to follow from Equation (1) that

$$\frac{1}{U}\frac{dU}{dT} = -\frac{1}{\eta}\frac{d\eta}{dT}.$$

For hydrating ions Darmois explains this difference as due to dehydration, occurring as the temperature rises, which will lead to a reduction in the Stokes radius. Actually, in that case

$$\frac{1}{U}\frac{dU}{dT} = -\frac{1}{\eta}\frac{d\eta}{dT} - \frac{1}{r_s}\frac{dr_s}{dT}.$$

in which $\frac{dr_s}{dT} < 0$. It is however difficult by this method to explain the difference between $\frac{1}{U}\frac{dU}{dT}$ and $-\frac{1}{\eta}\frac{d\eta}{dT}$ in the case of nonhydrating ions: it would have to be associated with $\frac{dr_s}{dT} > 0$.

The phenomenon of ionic hydration in aqueous solutions should be regarded from a different point of view, not having its origin in the concept of the binding by the ions of a particular number of water molecules, A more general approach to the study of the state of ions in aqueous solutions should be developed. The elucidation of the question of the binding by the ions of this or that number of water molecules should arise from such an approach only in the form of a deduction. It is possible that a general approach of this kind could be found by an examination of the effect of the ions on the thermal, particularly translational, motions of the water molecules that are nearest to them in the solution *. It will be evident that fairly firm binding by the ions of any number of water molecules will be associated with a considerable enfeeblement of this movement.

Action of Ions on the Translatory Movement of Water Molecules

Interaction of ions with the nearest water molecules in the solution causes the potential energy of these molecules to differ from that of water molecules in water, and there is therefore a difference in the heights of the potential barriers around the temporary equilibrium positions of water molecules in the vicinity of ions and of those of water molecules in a purely "aqueous" environment. The action of ions on the viscosity of water stands in direct relation to this. This action, as previously pointed out [5], consists in the change brought about by the ions in the activation energy of viscous flow of the water molecules that are the main constituents of the ionic environment in the change in the heights of the corresponding potential barriers. Thus it consists in the action of ions on the translatory movement of these molecules. It has been noted that ions affect the viscosity of water in different ways: small singly charged and multicharged ions increase the viscosity, and large single-charged ions reduce it. Consequently, ions act in different ways also on the translatory movement of the nearest water molecules. The small singly charged and multicharged ions (for example Li^+, Mg^{2+}, Ca^{2+}, hydrating ions) enfeeble this movement: if τ_1 is the mean time occupied by water molecules in equilibrium positions in the coordination layer of an ion, and τ is the corresponding time for pure water, then for such ions $\tau_1 > \tau$. On the other hand, a number of ions (for example K^+, Cs^+, Cl^-) increase the translatory movement of the nearest water molecules. For such ions $\tau_1 < \tau$. Water molecules in their vicinity become more mobile than they are in pure water. This phenomenon has been called "negative hydration" [6]. Watari [7] came to a similar conclusion as a result of investigations into questions of diffusion in solutions of electrolytes.

This concept of the effect of ions on the translatory movement of the nearest water molecules is in accord with the dependence of the activity coefficient of water in solutions of electrolytes on concentration. It is readily shown that the enfeeblement of the translatory motion of water molecules (reduction in their potential energy, rise in the negative potential) must lead to reduction in the activity coefficient of water and, on the other hand, intensification of the translatory motion (increase in potential energy) must lead to an increase. It has been shown that whereas activity coefficients of water in solutions of electrolytes having hydrating cations are less than unity (with the exception of a short low-concentration range), the activity coefficients of water in the case of cations showing negative hydration (K^+, Rb^+, Cs^+) are greater than unity over a considerable range of concentration [8].

The concept of negative hydration is not contradictory to the fact that the hydration of ions is always accompanied by the evolution of fairly large amounts of energy (high heats of hydration for ions). Actually, the energy of hydration of an ion may be divided into two parts: that conditioned by interaction of the ion with water molecules of its environment, and that conditioned by interaction with the remaining molecules. The first part may be either a reduction or an increase (negative hydration) in energy. However, the second part is always a reduction occurring in the ion-water system during dissolution of the ion, i.e. it always corresponds to evolution of energy. Although the energy of the interaction of an ion with a separate water molecule that does not form part of its immediate environment is very small, the total energy summed over many molecules attains high values; a considerable part of the heat of hydration of the ion is associated with it [9,10].**

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* In accord with the concepts, now fairly firmly established, concerning the nature of the thermal movement of particles in liquids (particularly water molecules in water), it is considered that this movement consists of vibrations about certain temporary positions of equilibrium and intermittent jumps from one equilibrium position to another, neighboring one (translatory movement) [4]. At a given temperature the translatory movement depends on the heights of the potential barriers surrounding the temporary equilibrium positions of the particles; it is characterized by the mean time occupied by a particle around one equilibrium position. In the present paper an examination is made of the translatory movement of water molecules relative to ions, which is characterized by the mean time occupied by water molecules in temporary equilibrium positions in the coordination layer of the ion.

** This follows from the calculations of Moelwyn-Hughes [10] on heats of ionic hydration if it is assumed that the coordination number for all ions in aqueous solutions is 4, which, according to the author, gives results that are just as satisfactory as the value of 6 that he assumes.

In order to make a quantitative examination of the effect of ions on the translatory motion of the nearest water molecules it is necessary to evaluate, at least approximately, the ratio τ_1/τ for individual ions.* If the height of the potential barrier surrounding the temporary equilibrium positions of water molecules in water is $\underline{E}$ (per mole of water), then $\tau = \tau_0 \cdot e^{\frac{E}{RT}}$ [4]. If the ion changes the value of E to E + ΔE, then in the vicinity of such an ion

$$\tau_1 = \tau_0 e^{\frac{E + \Delta E}{RT}} = \tau \cdot e^{\frac{\Delta E}{RT}}$$

and therefore

$$\frac{\tau_1}{\tau} = e^{\frac{\Delta E}{RT}} \tag{2}$$

Hence, in order to evaluate the ratio $\frac{\tau_1}{\tau}$, it is sufficient to evaluate the value of ΔE, the change produced by the ions in the potential barrier surrounding the temporary equilibrum positions of water molecules, or the change in the activation energy of viscous flow for these molecules. For the evaluation of ΔE, Stoke's law may be used.

The resistance experienced by an ion in moving in the solution is determined mainly by the activation energy of viscous flow of the water molecules immediately surrounding the ion. In this connection, η in Equation (1) must be understood as the viscosity of the water in the immediate vicinity of the ion and will have some value η_i that differs from the viscosity of pure water. The quantity of η_i is evidently the viscosity that water would have if the activation energy of the viscous flow of its molecules were the same as that of molecules comprising the im mediate environment of an ion. The quantity $\underline{r}$ must be taken as the crystallographical radius of the ion (r_c). Equation (1) may then be written:

$$U \eta_i r_c = \text{const}; \tag{1'}$$

and it permits η_i to be found (we note that $\frac{\eta_i}{\eta} = \frac{r_s}{r_c}$). The viscosity is related to the activation energy of viscous flow of molecules (E per mole) by the formula of exponential form, $\eta = Ae^{\frac{E}{RT}}$. Hence, approximately,

$$\eta_i = Ae^{\frac{E + \Delta E}{RT}}$$

and

$$\frac{\eta_i}{\eta} = e^{\frac{\Delta E}{RT}} \tag{3}$$

(η is the viscosity of pure water). Comparing Equations 3 and 2, we see that

$$\frac{\tau_1}{\tau} = \frac{\eta_i}{\eta}. \tag{4}$$

Having determined η_i from Equation (1'), it is possible with the aid of Equation (3) to evaluate the value of ΔE for various ions: $\Delta E = RT \ln \eta_i/\eta$. Thus for the ions Li^+, Na^+, K^+, and Cl^-, ΔE has the respective values of + 0.6, + 0.3, −0.1, and −0.2 kcal/mole of water.

In order to evaluate ΔE, use may also be made of experimental data on temperature coefficients of electrochemical ionic mobility. It is then necessary to postulate that the ionic radius in solution has the crystallographic value and that Stokes' law may be applied to the movement of ions in solution. It is sufficient to suppose that $\underline{r}$ is independent of temperature and that the coefficient of friction for movement of the ion is expressed by the formula $F = \eta\,\varphi(r)$, where φ is any function of $\underline{r}$ that is independent of temperature. As shown previously [6], the following relation is then obtained between the temperature coefficients of ionic mobility and the viscosity of water:

$$\frac{1}{U}\frac{dU}{dT} = -\frac{1}{\eta}\frac{d\eta}{dT} + \frac{\Delta E}{RT^2}. \tag{5}$$

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* In the present work, singly charged ions are examined.

Equation (5) permits, among other things, a very simple interpretation of the difference (Darmois [3]) between $\frac{1}{U}\frac{dU}{dT}$ and $-\frac{1}{\eta}\frac{d\eta}{dT}$, which was referred to at the beginning of this paper. Actually, if $\Delta E > 0$ (hydrating ions), then $\frac{1}{U}\frac{dU}{dT} > -\frac{1}{\eta}\frac{d\eta}{dT}$, and if $\Delta E < 0$ (negative hydration), then $\frac{1}{U}\frac{dU}{dT} < -\frac{1}{\eta}\frac{d\eta}{dT}$.

An approximate evaluation of ΔE by Equation (5) for various ions gives, for example for Li^+ and Cl^- [6], the values $\Delta E_{Li^+} \approx$ 0.4 kcal/mole of water and $\Delta E_{Cl^-} \approx -0.4$ kcal/mole of water. Thus, the evaluation of ΔE by the two methods described yields fairly close values. In any case it may be concluded that a correct indication of the order of ΔE is given.

By the use of these evaluations of ΔE, or simply by the aid of Equation (4), the ratio $\frac{\tau_1}{\tau}$ may be determined for various ions. For K^+ and Cl^- τ_1 is about 0.9τ and 0.6τ respectively, and for Li^+ and Na^+ it is 3.0τ and 1.8τ respectively.* The value of τ_1/τ is evidently a quantitative expression of the "binding" by the ions of the nearest water molecules in the solution. It should be noted that it is doubtful whether it is possible to speak of permanent hydration in the case of dissolved ions**. Rejection of the concept of permanent hydration is characteristic of the approach to the treatment of specific heats of ions in aqueous solution developed in the work of Kapustinsky [11].

As already noted, in the study of the state of ions in aqueous solutions, great importance is to be attached to the coordination numbers of ions in solutions — the mean numbers of constantly interchanging water molecules that comprise the immediate environments of ions in aqueous solutions. It has been established that the coordination numbers of ions in dilute aqueous solutions are close to the mean coordination number of water molecules in water [12,13]. It follows that the structure of water itself has a determining significance in the formation by water molecules of the equilibrium environment of ions in solution, which is undoubtedly related to the dynamic nature of this environment (constant exchange of water molecules around the ions). The extremely great importance of the structure of water in the phenomenon of ion hydration in aqueous solutions is emphasized by the existing data on the temperature dependence of the integral heats of solution of electrolytes [14,15].

Although the coordination numbers of ions in dilute aqueous solutions approximate to four, the density of the distribution of water molecules around ions is different for different ions (the sizes of the ions differ). It has been shown previously that this density characterizes the hydration of individual ions in solution [12].

Dividing Line between Hydrating and Nonhydrating Singly Charged Ions

The difference between the potential barriers surrounding the temporary equilibrium positions of water molecules in water and those in the vicinity of ions is related to the change produced by the ions in the potential energy of the nearest water molecules. It is clear that the raising of potential barriers ($\Delta E > 0$) is peculiar to ions that reduce the potential energy of the nearest molecules (increase their negative potential); on the other hand, the case $\Delta E < 0$ (negative hydration) corresponds to increase in the potential energy of the nearest molecules.

The change produced by ions in the potential energy of the nearest water molecules may be treated by the aid of the concept of the structure of dilute aqueous solutions of electrolytes based on estimations of the coordination numbers of ions in solutions [13]. When this is done it is found that there is a fundamental dividing line between hydrating and nonhydrating singly charged ions, i.e., a certain limiting value of the crystallographic ionic radius such that singly charged ions having radius less than this value are hydrating ions (reduce the potential energy of the nearest water molecules), and those having radius greater than this value are nonhydrating ions (increase the potential energy of the nearest molecules).

Bernal and Fowler [16] in an examination of this question start from the following considerations: the water molecule in water has four immediate neighbors, whereas the water molecule in the coordination layer of the ion has three immediate neighbors — the ion and two water molecules (cations are under consideration). Consequently, true hydration, i.e. reduction by the ions of the potential energy of the nearest water molecules, occurs, according to Bernal and Fowler, when the reduction in the potential energy of a water molecule caused by an ion is greater than the reduction caused by two water molecules.

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* It may be noted that τ is of the order of 10^{-10} second.

** It has already been noted [6] that rejection of the concept of permanent hydration does not contradict the results of experiments on the transfer of water by ions during electrolysis.

TABLE

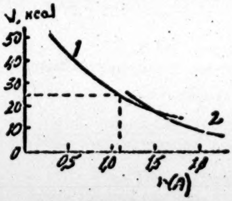
Crystallographic radii, ΔE and $\frac{\tau_1}{\tau}$ for singly charged ions *

Ion	r_c(A)	ΔE (kcal)	$\frac{\tau_1}{\tau}$
Li^+	0.78	$+0.6_3$	$3._8$
Na^+	0.98	$+0.3_4$	$1._8$
Ag^+	1.15	$+0.1_4$	$1._3$
K^+	1.33	-0.0_7	0.8_9
Tl^+	1.50	-0.1_5	0.7_7
Cs^+	1.65	-0.2_4	0.6_8
Cl^-	1.81	-0.2_5	0.6_5
Br^-	1.96	-0.3_3	0.5_9
I^-	2.20	-0.3_7	0.5_3

The energy of the interaction of an ion with a water molecule from its coordination layer that is oriented by it (it is here sufficient to consider electrostatic interaction) depends on the ionic radius and charge. The dependence of this energy (W) on the crystallographic radius of the ion, according to Bernal and Fowler, is given in the figure for singly charged ions. For ions of charge Z, W must be multiplied by Z. Hence all doubly and multi-charged ions are hydrating ions. The potential energy of a water molecule resulting from the action of the two nearest molecules is, according to Bernal and Fowler, about 15 kcal, and "true" hydration therefore occurs for ionic radii of up to 1.6 A. Among the alkali-metal cations, according to Bernal and Fowler, the only ion that increases the potential energy of the nearest water molecules in this way is Cs^+. This conclusion agrees with the results of their calculation of the supplementary energy of coordination by ions of water molecules of the solution. However, it is contrary to a number of facts that indicate that negative hydration is already found in the ion K^+.

Inasmuch as it has been established that the coordination numbers of ions in dilute aqueous solutions approximate to four [12], it is possible to give a treatment of the effect of ions on the potential energy of the nearest molecules of water in the solution by placing the ion in one of the "coordination positions" in the structure of water. In so doing, the difference in radius between the ions and water molecules may be neglected, mainly because in the region that is of interest (near to the limiting value of the radius that divides singly charged ions into hydrating and nonhydrating) this difference is small.

Replacement in the water structure of a water molecule by an ion without reorientation of the nearest molecules can lead only to an increase in the potential energy of these molecules. Actually, the orientation of water molecules in the water structure relative to a coordination position that is occupied by an ion is such that the change, due to interaction with the ion, in the potential energy of the water molecules that are nearest to the ion is on the average zero: the four molecules are oriented in pairs relative to the ion by means of their opposite poles**.



Dependence of the electrostatic energy of the interaction of ions with molecules oriented by them on the ionic radius: 1) cations; 2) anions.

However, the fact that the ion occupies a coordination position in the water structure leads to absence in the water molecules nearest to the ion of one of the four H_2O-H_2O bonds. If the energy of this bond is e kcal/mole, then owing to the introduction of the ion the potential energy of its nearest water molecules (if they are reorientated by the ion) will be increased by e kcal.

The molecule that is nearest to the ion has four neighbors — the ion, and three water molecules not entering into the immediate environment of the ion, with which it is bound by three bonds of energy e. Hence the reorientation of such a molecule by the ion leading to the rupture of these three bonds will evidently occur if $W > 3e$. However, this is still insufficient to cause the ion to reduce the potential energy of the nearest water molecules: the reduction in potential energy during reorientation must be greater than e (the increase in potential energy associated with the fact that the adjacent coordination position in the water structure is occupied by an ion), i.e. we must have

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* The values of ΔE and τ_1/τ refer to 18°. The second significant figure in these values is mainly of calculation significance.

** In any case the mean is small and may be taken as equal to zero.
The considerations here advanced may be illustrated by a much simplified scheme for the replacement of the water molecule in the water structure by an ion: a greatly simplified picture of the arrangement of molecules in water may be represented in a plane in the form of circles in contact arranged so that every circle touches four others (arranged, for example, at the intersections of a square-mesh net). The poles of the water molecules must be arranged so that unlike poles are in contact. One circle is to be taken as the ion. Such a scheme
(Footnote continued on next page)

$$W - 3e > e \text{ or } W > 4e.$$

This value of W defines the boundary between ions that reduce and ions that increase the potential energy of the nearest water molecules (between hydrating and nonhydrating ions). In the range $4e > W > 3e$ there is reorientation by the ions of the nearest water molecules, but the ions increase the potential energy of these molecules. When $W < 3e$ the ions increase the potential energy of the nearest water molecules and do not reorient them.

The dependence of the energy W on the crystallographic radius of the ion is represented by the curve shown in the figure. The energy of the bond H_2O-H_2O in water (e), according to Eley and Evans [9], is approximately 5.2 kcal/mole (6.2 + 4.2/2; only electrostatic interaction is considered). According to Pople [17], the most rigorous treatment of the electrostatic energy of the H_2O-H_2O bond in water gives 6.0 kcal/mole. We shall assume that e is 6.0 kcal/mole. The dividing line between hydrating and nonhydrating ions is then determined by a value of W of $6 \cdot 4 = 24$ kcal. On the W(r) curve a value of r = 1.1 A corresponds to this value of W.

The limiting value obtained for the radius agrees in general with the results of the examination of the effect of ions on the translatory motion of the nearest water molecules, as can be seen from the table. It is confirmed also by values of the temperature coefficients of electrochemical mobility for singly charged ions:

$$\frac{1}{U}\frac{dU}{dT} > -\frac{1}{\eta}\frac{d\eta}{dT} \quad \text{for } Li^+ \text{ and } Na^+ \; (\eta \text{ is the viscosity of water}).$$

$$\frac{1}{U}\frac{dU}{dT} < -\frac{1}{\eta}\frac{d\eta}{dT} \quad \text{for } K^+, Cs^+, Cl^-, Br^- \text{ and } I^-.$$

The range $4e > W > 3e$ corresponds to range of ionic radii from 1.1 to 1.5 A. It should be noted that e and W(r) are in the nature of evaluations.

SUMMARY

1. The effect of ions in aqueous solutions on the translatory motion of the nearest water molecules has been examined. Ions such as Mg^{2+}, Ca^{2+}, Li^+, and Na^+ reduce this motion ($\tau_1 > \tau$). A number of ions (for example, K^+, Cs^+, Cl^-) increase it ($\tau_1 < \tau$).

2. It has been shown that the mean period occupied by molecules of water in temporary equilibrium positions near to Li^+ and Na^+ ions is approximately 3.0τ and 1.8τ; the values near to K^+ and Cl^- are 0.9τ and 0.6τ.

3. It has been shown that there is a certain limiting value for the crystallographic radius which divides singly charged ions into hydrating and nonhydrating.

4. The structure of water is of highly fundamental significance in the phenomenon of ion hydration in dilute aqueous solutions.

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DETERMINATION OF THE DISTRIBUTION COEFFICIENTS OF RADIUM AND OF ITS ISOTOPE ThX BETWEEN MELT AND CRYSTALS OF CALCIUM NITRATE

V. G. Khlopin*, V. R. Klokman, and E. G. Pekelnaya

The anhydrous nitrates of calcium, strontium, barium, and lead, which crystallize in the form of regular octahedra, form, as is well known, an isomorphous group.

The distribution coefficient of radium in the crystallization of the solid phase from aqueous solution has been determined for only three members of this group, the nitrates of barium [1], strontium [2] and lead [3]. In all three cases the distribution coefficient D was found to be less than unity, which indicates that enrichment in the micro component occurs in the solid phase, for the distribution coefficient D is an expression of the number of times that the separating crystals are richer in micro component than the salt remaining in the solution:

$$D = \frac{x(100-y)}{y(100-x)}$$

where x and (100 − x) are the percentage amounts of radio element going into the crystals and remaining in the solution (or melt), respectively, and y and (100 − y) are the percentage amounts of the isomorphous salt going into the crystals and remaining in the solution (or melt), respectively.

The distribution coefficient has not been determined for calcium nitrate, because it crystallizes from aqueous solutions in the form of the tetrahydrate, which forms monoclinic crystals that are not isomorphous with anhydrous radium nitrate crystals. From the melt, however, calcium nitrate crystallizes as the anhydrous salt, isomorphous with radium nitrate, and so in this case the distribution coefficient of radium can be determined also for this fourth member of the isomorphous group.

The distribution coefficients of radium between melt and crystals were determined by us for the other three isomorphous salts in one of our previous investigations [4].

EXPERIMENTAL

In this work we used the method that we had already developed [4]. We studied the distribution coefficient of radium between melt and calcium nitrate crystals in the system $Ca(NO_3)_2-Ra(NO_3)_2-Na(NO_3)_2$.

Anhydrous calcium nitrate was prepared by drying the tetrahydrate carefully at 150°. Sodium nitrate was dried at the same temperature. As distributing micro component we used radium and its isotope ThX, the latter being prepared by collection of emitted atoms on a negatively charged plate. The activity of the melt before and after separation of the solid phase, which was required for the determination of the percent radium that had passed into the solid phase, was measured by the emanation method.

Before carrying out the distribution experiments, the melting curve of the $Ca(NO_3)_2-NaNO_3$ system was determined. Measurements were made for up to 70 mol. % of calcium nitrate: mixtures of greater calcium nitrate content begin to become opalescent, and the determination becomes inexact. According to our results, the eutectic melting point of this system is 230° and corresponds to 49.5 mol. % of calcium nitrate. Menzies and Dutt [5] give the eutectic temperature as 236° and the eutectic composition as 50 mol. % of calcium nitrate.

From the melting curve of the system the amount of separated solid phase [$Ca(NO_3)_2$] was calculated; so also were the compositions of the initial and final melts. The results of the experiments on the determination of the distribution coefficient of radium between melt and crystals of calcium nitrate are given in Table 1.

In Experiments 4 and 9 ThX was taken as micro component; in the remaining experiments, radium was taken. The experiments were carried out without stirring, for it has been shown that the rate of attainment of equilibrium for the case of the separation of a solid phase is independent of whether or not the melt is stirred [6]. Experiments 9 and 10 were carried out by the method of recrystallization of an excess of calcium nitrate in a

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* Deceased

TABLE 1

Distribution of Ra between Melt and Crystals of $Ca(NO_3)_2$

Expt. No.	Amt. of $Ca(NO_3)_2$ crystallized out (%)	Amt. of Ra transferred to solid phase (%)	D
1	30.0	27.0	0.9
2	40.0	36.5	0.9
3	40.0	35.4	0.8
4	45.0	45.4	1.0
5	52.3	56.2	1.1
6	52.3	56.7	1.2
7	52.3	53.4	1.0
8	52.3	55.4	1.2
9	64.0	63.7	1.0
10	74.3	74.9	1.0
		Mean . . .	1.0

TABLE 2

Distribution Coefficients of Radium between Melts and Crystals of Nitrates of Bivalent Metals

Isomorphous salt	D
$Ba(NO_3)_2$	0.4
$Sr(NO_3)_2$	0.4
$Ca(NO_3)_2$	1.0
$Pb(NO_3)_2$	1.0

melt of definite composition at a definite temperature over a period of four hours; this permitted an increase in the amount of solid phase separated, without rise in temperature. All the remaining experiments were carried out by the method of solid-phase separation from the saturated melt.

It will be seen from Table 1 that the distribution coefficient remains constant at the mean value of unity, independently of the amount of solid phase separated. The amount of solid phase varied from 30 to 74.3%. From these and our previous results on the distribution coefficients of radium between the melt and crystals of isomorphous salts, we may construct the following composite table (Table 2) for all four members of this isomorphous group.

It will be seen from Table 2 that in the case of the distribution of radium between the melt and crystals of barium and strontium nitrates, the distribution coefficient D is 0.4, i.e. in this case there is enrichment of the micro component of the melt. For the distribution of radium between melt and crystals of calcium and lead nitrates, D is unity, which indicates uniform distribution of the micro component between melt and crystals for these salts. Thus, in the distribution of radium between melt and crystals for the isomorphous salts, two interesting peculiarities are to be observed.

TABLE 3

Radii of Ions of Bivalent Metals

Element	Ionic radius R (A)	$R_{Ra}-R_{El}$	Difference in radii (% of the lesser)
Ra	1.52	–	–
Ba	1.43	0.09	6
Sr	1.27	0.25	20
Ca	1.06	0.46	43
Pb	1.32	0.20	15

The first peculiarity is that radium forms mixed crystals most readily not with its closest neighbors in the group – barium and strontium – but with further removed elements – calcium and lead; i.e. in this isomorphous group the propensity for the formation of mixed crystals with radium among the analogous elements does not follow the same order as the ionic radii (see Table 3).

The second peculiarity is that, in the systems that we have studied so far in which radium is distributed between melt and crystals of isomorphous salts, enrichment in radium of the solid phase has not been observed.

SUMMARY

1. The distribution coefficient of radium and of its isotope ThX between melt and crystals of calcium nitrate has been determined.

2. It has been found that also in this system the distribution of radium between melt and crystals of an isomorphous salt does not lead to enrichment of the solid phase in radium.

3. It has been shown that in the isomorphous group of Ca, Sr, Ba, and Pb nitrates radium readily forms mixed crystals with the nitrates of calcium and lead, but not with those of strontium and barium, its closest neighbors in the group.

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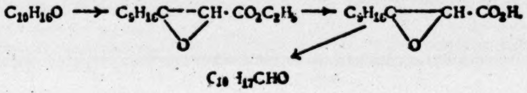
β-AMINO ACIDS

COMMUNICATION 34. SYNTHESIS AND CHARACTERIZATION OF β-AMINODECAHYDRO-2-NAPHTHALENEPROPIONIC ACID

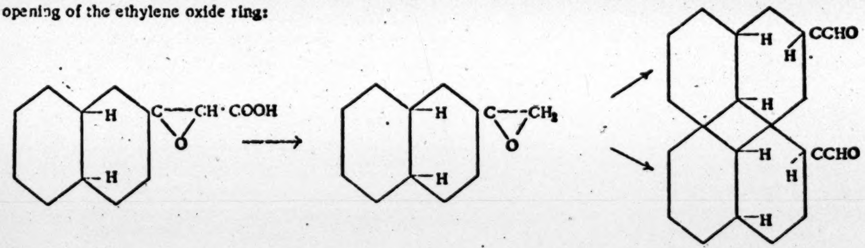
V. M. Rodionov and L. V. Antik

As starting material for the synthesis of β-(2-decalyl)-β-alanine (β-aminodecahydro-2-naphthalenepropionic acid), β-decalone (octahydro-2-(1H)-naphthalenone) was taken; this was obtained by oxidation of cis-β-decalol (cis-decahydro-2-naphthol), m.p. 105°. β-Decalone was condensed with ethyl chloroacetate by Darzens' method [1] to yield a glycidic ester, which on hydrolysis and decarboxylation gave decahydro-2-naphthaldehyde:



$$C_{10}H_{16}O \longrightarrow C_9H_{16}\underset{O}{C{-}{-}CH}\cdot CO_2C_2H_5 \longrightarrow C_9H_{16}\underset{O}{C{-}{-}CH}\cdot CO_2H \longrightarrow C_{10}H_{17}CHO$$

The synthesis of the β-decalyl-β-amino acid was brought about by condensation of the aldehyde with malonic acid according to the method of Rodionov and coworkers [2], the yield of β-amino acid was about 50%, based on the amount of aldehyde taken for reaction. At the same time, a mixture of unsaturated acids of the β-decalylacrylic type was isolated. The syntheses and the purification of the substances obtained were rendered very difficult by the fact that in the reactions studied mixtures of difficultly separable stereoisomeric forms could arise. The formation of these were possible, evidently, because the decahydro-2-naphthaldehyde used was itself a mixture of two stereoisomeric forms, produced during decarboxylation of the glycidic acid and subsequent opening of the ethylene oxide ring:

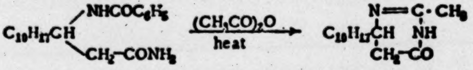


The present investigation is not concerned with this interesting reaction, which will be the subject of a future study.

The possibility of producing isomeric forms was noted already in the early stages of the work, but attempts to separate these forms, even by repeated tedious recrystallizations that greatly reduced the yields of the desired substances, were not always successful. The first successful separation of this sort was effected by the aid of acid chlorides of N-benzoyl derivatives of β-(2-decalyl)-β-alanine. The isomeric acid chlorides have different solubilities in ether, and the amides obtained from them are sharply distinguished by their melting points, 210-212° and 250 and 252°. Mixed melting point tests show depressions. The corresponding isomers of N-benzoyl-β-(2-decalyl)-β-alanine were prepared by cautious hydrolysis of the amides.

In order to characterize the new β-amino acids, attempts were made to synthesize their N-carbamoyl derivatives (the related ureido acids), related hydrouracils, and also, by the Curtius reaction, 3-benzoyl-4-(2-decalyl)-2-imidazolidinones and the corresponding decalylimidazolidinones. When carrying out the Curtius reaction it was again found possible, owing to the different solubilities of the benzoyldecalylimidazolidinones in benzene, to separate two isomers, m.p. 213-215° and 173.5-175°. The isomer of m.p. 213-215° gave 4-(2-decalyl)-2-imidazolidinone.

The transacylation reaction discovered previously in our laboratory, in which amides of benzoylated acids are heated with acetic anhydride [3], was carried out also on the amide of β-(2-decalyl)-β-alanine; instead of cyclization to 6-(2-decalyl)-5,6-dihydro-2-phenyl-4(3H)-pyrimidinone, the corresponding 2-methyl compound was isolated:



The ureido acid, hydrouracil, hydrazide, and azide were obtained in good yields by the usual methods (see Experimental).

EXPERIMENTAL

Preparation of the Glycidic Ester. Finely ground sodamide (18.5 g) was introduced under mechanical stirring at 15-20° into a mixture of cis-β-decalone (octahydro-2(1H)-naphthalenone) (60 g) (prepared by oxidation of cis-decalol, m.p. 105°, with chromic acid), ethyl chloroacetate (48.5 g), and dry benzene (90 ml). After being stirred at this temperature for three hours, the reaction mixture was poured onto ice (280 g); the oil formed was separated, and the aqueous layer was extracted twice with benzene (100 ml each time). The benzene extract was mixed with the separated oil, and the mixture was washed carefully with water until it reacted neutral; it was then dried over sodium sulfate. Benzene was removed, and the residue was vacuum-distilled, yielding the glycidic ester (53.8 g, 57.3%), b.p. 178-191°/20 mm. At the same time, unchanged β-decalone (15.9 g, 26.5%) and a high-boiling (about 200°/20 mm), possibly polymeric substance (which was not investigated) (6.7 g) were isolated.

Found %: C 70.45; 70.66; H 9.37; 9.39
$C_{14}H_{22}O_3$. Calculated %: C 70.54; H 9.31.

Preparation of Decahydro-2-naphthaldehyde. The glycidic ester (70.6 g) was heated with a 20% potash solution (500 g) under mechanical stirring for 60 minutes. The solution obtained was cooled and carefully acidified with 18% hydrochloric acid; the glycidic acid, which separated as an oil, was then extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4. The solvent was driven off, and the residual gel-like mass was heated under reduced pressure, when the aldehyde formed distilled over; the fraction 80-130°/8mm was collected. Refractionation yielded decahydro-2-naphthaldehyde (115-121°/13 mm) (about 26 g, 51.5 %). The semicarbazone, which crystallized from alcohol in rectangular plates, had m.p. 173-175°.

Found %: N 19.35; 19.40
$C_{12}H_{21}ON_3$. Calculated %: N 18.83

Preparation of β-(2-Decalyl)-β-alanine (β-Aminodecahydro-2-naphthalenepropionic Acid). Decahydro-2-naphthaldehyde (8 g) was mixed at 0° with a 7% alcoholic solution of ammonia (12 ml, i.e. 10% excess), and malonic acid (5 g) was added to the white oily mass formed. The reaction mixture was heated on the water bath for five hours under reflux, and the crystalline mass obtained after removal of the alcohol was extracted with hot water. The insoluble residue was dried and washed with boiling benzene. The total yield of amino acid of m.p. 203-205° was 5.2 g, i.e. about 48% calculated on the amount of decahydronaphthaldehyde taken. Recrystallization from alcohol gave needles, m.p. 211°.

Found %: C 69.22; 69.30; H 10.39; 10.52; N 6.59; 6.43
$C_{13}H_{23}O_2N$. Calculated %: C 69.27 H 10.29 N 6.22

Unsaturated acids present were extracted from the benzene solution by means of a 5% sodium carbonate solution. From the total amount (105 g) of decahydro-2-naphthaldehyde taken for all the preparations carried out a yield of 14.5 g of unsaturated acids was obtained. The product as first obtained was an oil, which by fractional distillation under reduced pressure yielded a thick straw-yellow liquid over the range 210-215° at 23 mm. The acid was further purified through the sodium salt. The oil that separated on acidification gradually solidified and, after recrystallization from petroleum ether, it melted at 72-92°. The wide melting range is to be explained by the presence of a mixture of isomers. Values of 212.9 and 214 were found for the equivalent weight; the value calculated for $C_{13}H_{20}O_2$ is 208.16. The mixture of unsaturated acids was found to decolorize bromine water and permanganate solution. It was not studied further.

Preparation of the Benzoyl Derivative. To a solution prepared by dissolving β-(2-decalyl)-β-alanine (15 g) in a 10% caustic potash solution (110 g), benzoyl chloride (7.9 ml) was added at 2° over 15 minutes.

The reaction mixture was stirred for four hours, the temperature being gradually raised to 40° (the temperature was at about 40° for the last two hours). The solution was cooled and washed with ether, and the aqueous layer was acidified with hydrochloric acid (to Congo Red). The slowly crystallizing oil that separated was carefully washed with boiling water and cooled. The product was N-benzoyl-β-(2-decalyl)-β-alanine (18.8 g, 85.7 %), m.p. 140-143°.

Found %: N 4.25; 4.10

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

The substance obtained was a mixture of isomers, for after it had been recrystallized three times from benzene, its melting point rose to 204-206° and did not change further. Analysis for nitrogen showed that the substance purified in this way was also N-benzoyl-β-(2-decalyl)-β-alanine ($C_{20}H_{27}O_3N$), i.e., this treatment had yielded one of the stereoisomeric forms in the pure state.

Found %: N 4.68; 4.59

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

Preparation of the Isomeric Amides of N-Benzoyl-β-(2-decalyl)-β-alanine. The mixture of the cis and trans isomers of the benzoyl derivative of the amino acid having m.p. 140-143° (18.3 g) was heated with thionyl chloride (19.9 g) for 3 hours 30 minutes at 40-42°. The excess of thionyl chloride was driven off under reduced pressure, and the hard glassy mass of acid chlorides obtained was treated with dry ether. At first complete dissolution occurred, and then, from the solution obtained, a white crystalline precipitate came down. It was filtered off and washed with dry ether. This precipitate and the ether solution were each treated with dry ammonia under cooling. The ether-insoluble acid chloride yielded an amide of m.p. 200-205° (2.63 g), and after it had been recrystallized twice from alcohol, its melting point rose to 210-212° and did not change further.

Found %: C 73.29; 73.38; H 8.75; 8.82; N 8.55; 8.63

$C_{20}H_{28}O_2N_2$. Calculated %: C 73.12; H 8.60; N 8.53

Action of ammonia on the ether-soluble acid chloride yielded an amide of m.p. 180-205° (12.82 g). After two recrystallizations the melting point rose to 250-252°.

Found %: C 73.23; 73.03; H 8.69; 8.76; N 8.86; 8.81.

In a mixed test on the two amides the melting point fell to 199°.

The total yield of pure recrystallized amides was about 40%.

Hydrolysis of the Amide of m.p. 210-212°. The amide (0.1 g) was heated for 5-6 hours with 12% hydrochloric acid (10 ml). Cooling of the solution yielded the benzamido acid (0.08 g), completely soluble in alkalis. After it had been recrystallized three times from alcohol, it melted at 186-188°. Analysis for nitrogen confirmed its structure.

Found %: N 4.62; 4.67

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

In a similar manner (by means of concentrated hydrochloric acid) the amide of m.p. 250-252° was hydrolyzed. The benzamido acid obtained was recrystallized three times from benzene, but did not melt sharply (170-175°).

This product was evidently a contaminated preparation of the benzamido acid isomer referred to above.

Found %: N 4.36; 4.50

A mixed test on the two preparations gave a depressed melting point of 155°.

Action of Acetic Anhydride on the Amide of m.p. 210-212°. A mixture of the amide (0.62 g) and acetic anhydride (4.3 ml) was boiled gently for 10-12 hours. The solution obtained was cooled and filtered from the small amount of unchanged amide (0.02 g), and the excess of acetic anhydride was removed from the filtrate by heating it under reduced pressure. The residue was boiled with water, cooled, and extracted with ether. The ether extract was washed with a weak solution of alkali and then with water; it was dried over Na_2SO_4. The ether was removed yielding a substance (0.36 g) of m.p. 116-129°. The melting point, after three recrystallizations from ether, was 158-159.5°. The analysis and properties of the substance obtained indicated it to be a (2-decalyl)-dihydromethyl-4(3H)-pyrimidone, formed as a result of a transacylation reaction.

Found %: N 11.05; 10.99
$C_{15}H_{24}ON_2$. Calculated %: N 11.29

This reaction was confirmed also by an examination of the aqueous layer from which benzoic acid was isolated (0.23 g, almost theoretical yield).

Preparation of N-Carbamoyl-β-(2-decalyl)-β-alanine (Decahydro-β-ureido-2-naphthalenepropionic Acid). Sodium cyanate (0.35 g) was added to a boiling solution of β-(2-decalyl)-β-alanine (1 g) in water (16 ml), and heating was continued on a boiling water bath for 3-4 hours. When the solution was cooled and acidified, a rapidly crystallizing oil came down (1 g, about 84 %). The ureido acid, after recrystallization from alcohol (rectangular plates), melted at 205-206°.

Found %: N 10.59; 10.63
$C_{14}H_{24}O_3N_2$. Calculated %: N 10.45

Preparation of 6-(2-Decalyl)-hydrouracil. The ureido acid (0.06 g) was heated with hydrochloric acid (15 ml, sp. gr. 1.17) for three hours over a gauze. At first there was complete solution, and then a crystalline precipitate formed, granular at first, turning gradually into leaflets. Concentration and cooling gave crystals of the hydrouracil compound (about 0.05 g, about 85%). After recrystallization from alcohol, the decalylhydrouracil melted sharply at 269-270°.

Found %: N 11.51; 11.54
$C_{14}H_{22}O_2N_2$. Calculated %: N 11.20

Preparation of the Ethyl Ester of N-Benzoyl-β-(2-decalyl)-β-alanine. 1) Hydrogen chloride was passed for 5-6 hours at 60-75° into a solution of the benzoylated amino acid (2.4 g) in absolute alcohol (30 ml); the reaction mixture was then cooled to 0°, hydrogen chloride was passed to saturation, and the mixture was set aside overnight. The solvent was vacuum-distilled off, and the residue was washed with water and extracted with ether. The ether extract was washed with a weak solution of sodium bicarbonate and with water, and was dried over anhydrous sodium sulfate. After removal of ether, a rapidly crystallizing oil (2.6 g, m.p. 72-83°) remained; it melted after recrystallization from petroleum ether at 77-82° (2.46, about 94 %).

Found %: N 4.38; 4.25
$C_{22}H_{31}O_3N$. Calculated %: N 3.92

2) An identical product was obtained by benzoylation of the ethyl ester of β-(2-decalyl)-β-alanine, the latter, which was prepared in the usual way, being dissolved in five times its weight of pyridine and treated with a small excess of benzoyl chloride at -5°. After prolonged standing at room temperature, the reaction mixture was washed with water and hydrochloric acid and extracted with ether. The ether extract was neutralized with a solution of sodium bicarbonate, washed with water, and dried over sodium sulfate. The rather thick oil that remained after removal of the solvent rapidly solidified; it melted after recrystallization from petroleum ether at 79-83° and did not depress the melting point of the ester prepared by the first method.

Preparation of the Hydrazide of N-Benzoyl-β-(2-decalyl)-β-alanine. The ethyl ester of N-benzoyl-β-(2-decalyl)-β-alanine (5.3 g) was added gradually (in four portions) to heated hydrazine hydrate (2.25 ml); some absolute alcohol (6 ml) was added to the last portion of the ester. The solution obtained was boiled gently for 60-75 minutes; an almost solid crystalline mass formed, and some absolute alcohol (5-6 ml) was therefore added and heating was continued for a further 30-40 minutes on a boiling water bath. The mixture was cooled, and the precipitate was filtered off and washed on the filter successively with water, alcohol, and ether. The hydrazide obtained (4.54 g, 89%) melted at 182-196°; after three recrystallizations from alcohol the melting point rose to 201.5-204.5°.

Found %: N 12.13; 12.31
$C_{20}H_{29}O_2N_3$. Calculated %: N 12.24

Preparation of N-Benzoyl-β-(2-decalyl)-β-alanine Azide and of 3-Benzoyl-4-(2-decalyl)-2-imidazolidinone. The hydrazide of N-benzoyl-β-(2-decalyl)-β-alanine (1.75 g, m.p. 182-196°) was dissolved in 73-75% acetic acid (35 ml) and cooled to 0°. To this solution finely ground sodium nitrite (1.26 g) was added in 3-4 portions over a period of 15 minutes with shaking. The solution was allowed to stand for two hours at 0°, and ice water was then added; the precipitate of azide that formed was filtered off and washed with ice water on the filter until the odor of acetic acid disappeared. The preparation was well pressed between filter papers and was mixed without drying with 95 ml of absolute benzene and then heated. The whole of the water present distilled over with 50 ml of benzene: the condenser was then reset in the reflux position, a further 45-50 ml of benzene was added to the reaction mixture, and boiling was continued for a further four hours. The solution was filtered hot to remove mechanical contamination, and the filtrate was concentrated, about 50 ml of benzene being driven off. The solution, on being cooled, yielded white needles of m.p. 210-217° (0.7 g). After evaporation of the mother liquor to dryness and washing of the residue with a small amount of ether, a further 0.59 g of material of m.p. 167-173° was obtained.

Both compounds, according to their properties and elementary analyses, appeared to be 3-benzoyl-4-(2-decalyl)-2-imidazolidinones. Thus, by means of the Curtius reaction it was found possible to bring about separation of the two stereoisomeric forms. The first product after recrystallization from benzene melted at 213-215°.

Found %: N 8.68; 8.53

The second was recrystallized from alcohol and then melted at 174-175°.

Found %: N 8.34; 8.28

$C_{23}H_{26}O_2N_2$. Calculated %: N 8.59

A mixed melting-point test on the two benzoyldecalylimidazolidinones showed a small but definite depression. The total yield of benzoyldecalylimidazolidinones was 1.29 g (about 78% of the hydrazide).

Preparation of 4-(2-Decalyl)-2-imidazolidinone. Nonpurified benzoyldecalylimidazolidinone of m.p. 210-217° was taken for hydrolysis; it was heated with 20% caustic soda on a water bath for 4-5 hours. Hydrolysis did not go very readily, and a greatly contaminated imidazolidinone compound was obtained having an extended melting range. After repeated recrystallization from alcohol, 4-(2-decalyl)2-imidazolidinone, m.p. 254.5-253.5°, was obtained.

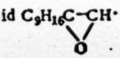
Found %: C 70.61; 70.37; H 10.23; 10.09; N 12.85; 12.73

$C_{13}N_{22}ON_2$. Calculated %: C 70.21; H 9.98; N 12.61

At the same time benzoic acid (about 64%) was isolated. Part of the benzoyl derivative remained unchanged even after a more prolonged heating with caustic soda.

SUMMARY

1. It has been established that by the decarboxylation of the glycidic acid $C_9H_{16}C\text{—}CH\cdot COOH$, obtained by Darzens' method from cis-decahydro-2-naphthol of m.p. 105°, a mixture of stereoisomeric decahydro-2-naphthaldehydes is formed; these have not been investigated further.



2. The synthesis has been effected, by Rodionov's method, of β-(2-decalyl)-β-alanine (β-amino-decahydro-2-naphthalenepropionic acid), which also appeared to be a mixture of isomers, the separation of which was not carried out.

3. By taking advantage of the different ether-solubilities of the acid chlorides of the N-benzoylated β-(2-decalyl)-β-alanines, the corresponding amides, m.p. 210-212° and 250-252°, were isolated.

4. The two amides were converted by careful hydrolysis into the isomeric N-benzoylated β-(2-decalyl)-β-alanines.

5. It has been shown that when the amide of N-benzoyl-β-(2-decalyl)-β-alanine is heated with acetic anhydride, a transacylation reaction occurs, and instead of 6-(2-decalyl)-5,6-dihydro-2-phenyl-4(3H)-pyrimidinone the corresponding 2-methyl derivative is obtained.

6. In order to characterize β-(2-decalyl)-β-alanine, the corresponding ureido acid and 6-(2-decalyl)-hydrouracil were prepared.

7. Esters and hydrazides of N-benzoyl-β-(2-decalyl)-β-alanine have been prepared, and, by means of the Curtius reaction, they have been converted into 3-benzoyl-4-(2-decalyl)-2-imidazolidinones and the corresponding 4-(2-decalyl)-2-imidazolidinone.

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CONVERSION OF PENTANE INTO LIQUID HYDROCARBONS AND GAS AT 250-360 ATMOSPHERES AND 400-500°

A. V. Topchiev, Ya. M. Paushkin, B. A. Krentsel, and I. M. Tolchinsky

It was shown in one of our investigations [1] that pentane may be converted catalytically into liquid hydrocarbons and gas at 20-80°. This reaction can be brought about in a similar way also for propane and butane. The present investigation is concerned with the conversion of pentane into liquid and gaseous hydrocarbons at comparatively high temperatures.

The reactions undergone by pentane may proceed in several directions.

1. Cracking of pentane. The thermal reactions of pentane resulting from cracking at 400-500° and at atmospheric pressure lead to the formation of gaseous products only [2]. The gas formed in four hours at 396° contains 2 % of hydrogen, 19% of methane, 24% of ethane, 22% of propene, 9% of butenes, 2% of butane, and 12% of pentane; it contains also an insignificant amount of ethylene and propane. The product obtained by cracking isopentane at 550° is of similar composition. In cracking, therefore, the main process is the splitting of the pentane molecule with formation of methane, ethane, and other gaseous hydrocarbons, but no liquid products.

2. Destructive alkylation. It was shown by Paushkin and Fleish [1] that isopentane on long contact (several months) at 15-20° with aluminum chloride as catalyst is converted into gas and liquid hydrocarbons in the C_6–C_9 range. This process can be effected also in the course of an hour at 80° and 8-10 atm. in presence of 8-10% of aluminum chloride. The liquid distillate formed in this reaction distills over in the range 35-130° and corresponds in amount to 30-45% of the original isopentane. The gas formed corresponds in amount to 35-55% of the isopentane and contains about 60% by volume of isobutane. The liquid reaction products have an unsaturated character; the hexane fraction contains 2,2-dimethylbutane and 2-methylpentane.

This reaction may be regarded as a combined process in the first stage of which splitting (cracking) of isopentane into alkenes and alkanes occurs; in the second stage the alkenes formed alkylate the original isopentane molecule. In the first stage energy is used, and in the second, energy is given up. As a result of the combined cracking and alkylation reactions the expenditure of energy necessary in the first stage is compensated, and the process becomes possible at low temperatures.

As already mentioned, the destructive alkylation of the gaseous hydrocarbons, propane and butane, can be brought about in a similar way to that of pentane. Results have been recently published on the destructive alkylation of propane, butane, and pentane in presence of BF_3 + HF as catalyst [3]. This catalyst acts similarly to aluminum chloride. The reaction with propane was carried out in an autoclave (47 atm. 85°, 2 hr.). The extent of conversion of the propane was 10%. The reaction products contained 5.7% of ethane, 82.8% of isobutane, and 11.5% of hydrocarbons bound by the catalyst.

The reaction was carried out with butane at 50° for 0.5-2 hours under a pressure of about 24 atm. over the same catalyst. Conversion of butane into liquid hydrocarbons attained 8.5%; about 50% of the original butane isomerized into isobutane. The destructive alkylation of pentane over BF_3 + HF proceeded with a conversion of 24%. The reaction was carried out at 85° under a pressure of 21 atm., but it was found that, in presence of 2% of pentene, the reaction temperature could be lowered to 32° for a period of contact with a catalyst of 30 minutes. Under these conditions 23-24% of the pentane was converted into high-boiling hydrocarbons.

3. Isomerization of pentane. Moldavsky and coworkers [4], in a study of the isomerization of pentane in presence of aluminum chloride, noted that, in addition to the main reaction product, isopentane, hexanes, mainly 2,2-dimethylbutane, were formed as by-products. The formation principally of 2,2-dimethylbutane was explained by the authors of this paper by the greater ease of methylation of the hydrogen of a tertiary carbon atom, as compared with that of hydrogens in other groups.

However, this hypothesis is doubtful, for it is difficult to explain from this point of view the fact, observed by them, of the formation of isopentane instead of the expected 2,2-dimethylpropane in the isomerization of butane in presence of aluminum chloride. The simultaneous formation of high-boiling hydrocarbons in the isomerization of pentane is pointed out also in other published papers [5]. Thus, isomerization of pentane is accompanied by destructive alkylation, leading to the formation of hydrocarbons boiling higher than the original pentane.

4. Formation and further reaction of pentane during thermal alkylation. Pentane and isopentane are formed during the thermal alkylation of propane by ethylene at 500° and 300 atm. [6]. The liquid reaction products consist of pentane and isopentane (73%) and a C_6–C_9 fraction (27%) containing about 15-20% alkenes. The gas formed in the thermal alkylation of propane with ethylene consists approximately of 50% methane, 20% ethane, and 30% butane (without considering unchanged propane and ethylene). Thus, in addition to the main reaction, alkylation of propane by ethylene to pentanes, destructive alkylation occurs, yielding hexanes, octanes, and nonanes. The gas formed is essentially methane.

EXPERIMENTAL

The experiments on the thermal conversion of pentane were carried out in a rotating autoclave, 500 ml in capacity. In this a pentane fraction (about 300 ml) was placed; it boiled in the range 32-38° and had d_4^{20} 0.6238; n_D^{20} 1.3575, and a bromine number of zero. The distillation curve of the initial fraction is shown in Figure 1. Thus, the pentane fraction used as raw material consisted essentially of n-pentane, and in future it will be referred to as pentane. The autoclave was heated by means of an electric furnace, and the temperature in the autoclave was measured and controlled within the set range by the aid of an alumel-chromel thermocouple connected to a PM-47 electronic galvanometer. At the end of the experiment the autoclave was cooled to room temperature and the gaseous reaction products were passed out of the autoclave through a system of traps, cooled by a cooling mixture to below 0°, in order to hold back pentane. The gas then passed through a gas meter, after which part of the gas proceeded to a gasholder for analysis and the remainder passed out into the atmosphere. The liquid reaction products in the autoclave consisted of a mixture of unchanged pentane and the higher-boiling liquid hydrocarbons formed. The unchanged pentane was distilled off through a fractionating column within the boiling limits of the original material, and the remaining, heavier hydrocarbons were fractionated through a column of 35 theoretical plates and investigated further as described below. The composition of the gas obtained in a number of pentane-conversion experiments was determined by fractionation through a low-temperature fractionation column.

Thermal Conversion of Pentane

The thermal conversion of pentane was carried out in absence of catalysts in the temperature range 350-450°. The effect of temperature on the progress of pentane conversion was investigated for constant duration of reaction (two hours). The results obtained are given in Table 1 and Fig. 2.

At 350° pentane did not undergo conversion, appreciable reaction commencing only at temperatures above 375°. It follows from the results given in Table 1 that the optimum temperature for the conversion of pentane into higher-boiling liquid hydrocarbons is in the range 450-460°, the corresponding pressure being 250-310 atm. At 480° and above, splitting of pentane with formation of a large amount of gaseous hydrocarbons takes place.

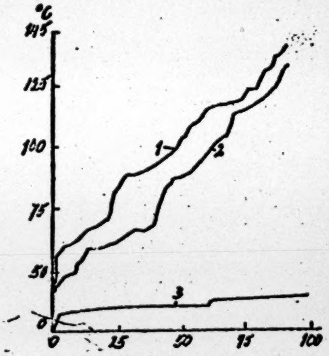

Fig. 1. Distillation curves for the conversion products of the pentane fraction and for the raw material: 1) thermal process; 2) aluminosilicate catalyst; 3) original raw material.

A further series of experiments was carried out with the aim of determining the effect of the duration of the reaction on the degree of conversion of the pentane. The results of this series of experiments are shown in Table 2 and are presented graphically in Figure 3.

As will be seen from the results cited, a sufficient degree of conversion into liquid products is attained in two hours; increase in the time to three hours increases the amount of gaseous products.

As a result of a number of successive experiments under optimum conditions (2 hrs., 450-455°, 300-350 atm) 450 g of liquid products boiling higher than the original pentane was accumulated. These products were fractionated and investigated as described below. The liquid product extracted from the autoclave had the following characteristics: d_4^{20} 0.6776; n_D^{20} 1.4046.

TABLE 1

Effect of Temperature on the Yield of Products of the Thermal Conversion of Pentane

Temp. of expt. (mean) (°C)	Pressure (mean) (atm)	Amt. of unchanged pentane (%)	Amt. of conversion products (%)	
			liquid	gaseous
350	200	100.0	0	0
375	218	33.9	6.0	–
415	230	81.2	14.1	4.7
453	260	66.5	22.1	11.4
460	310	64.2	23.2	12.6
480	510	39.3	16.2	44.5

TABLE 2

Effect of Time on the Degree of Conversion of Pentane

Reaction time (hr.)	Temperature (°C)	Pressure (mean) (atm.)	Amt. of unchanged pentane (%)	Amt. of reaction products (%)	
				liquid	gaseous
0.25	450	210	99.0	1.0	–
1.0	450	310	81.3	12.4	6.3
2.0	460	325	64.8	23.2	12.0
3.0	455	310	73.0	12.2	14.5

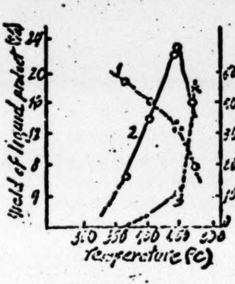

Fig. 2. Effect of temperature on the yield of products of the thermal conversion of the pentane fraction: 1) pentane; 2) liquid product; 3) gaseous product.

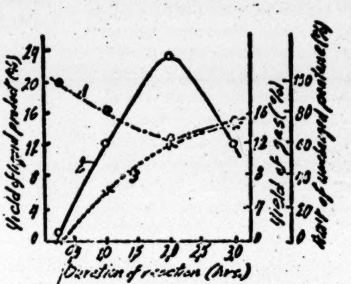

Fig. 3. Effect of time on the yield of products of the thermal conversion of the pentane fraction: 1) pentane; 2) liquid product; 3) gaseous product.

The product was fractionated through a column of 25 theoretical plates and consisted of 63% (by volume) of a fraction boiling up to 150°, called the gasoline fraction, and 37% of a fraction boiling above 150° and up to 300°. The specific gravity of the mixture of hydrocarbons boiling above 40° was $d_4^{20} = 0.7469$; n_D^{20} was 1.4238, the bromine number was 18.2, and the content of sulfonatables, determined by means of Kattwinkel's mixture, was 28 %.

The gasoline fraction had the following constants: d_4^{20} 0.7201; n_D^{20} 1.4087; bromine number 24.5; content of sulfonatables, determined by means of Kattwinkel's mixture, 8.3%. The octane number of this fraction, determined by the engine method, was 67 points.

Narrow fractions, separated by fractionation of the gasoline fraction through a column of 35 theoretical plates, were subjected to qualitative spectrum analysis, the Raman spectra being employed.*

The results of the analysis of the fractions obtained are given in Table 3.

Apart from the hydrocarbons indicated, an insignificant amount of unsaturated hydrocarbons was detected in all fractions. Thus, in the thermal conversion of pentane a variety of hydrocarbons is obtained, the formation of which is associated, evidently, with the reactions of destructive alkylation, cyclization, and cracking of pentane followed by polymerization of unsaturated hydrocarbons.

The gas formed in the thermal conversion of pentane was fractionated in a low-temperature fractionation apparatus in order to determine its composition. The results of the analysis are given in Table 4.

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* The spectrum analysis was carried out by M. V. Shishkina, and we take this opportunity of thanking her.

TABLE 3

Hydrocarbons Detected among the Products of the Thermal Conversion of Pentane*

Boiling range of fraction (°C)	Refractive index n_D^{20}	Hydrocarbons dectected
56-65	1.3810	2-Methylpentane, 3-methylpentane, 2,3-dimethylbutane
65-70	1.3891	Hexane, 2-methylpentane
80-90	1.3961	Benzene, 3-methylhexane, 2-methylhexane. 2,4-dimethylpentane, 2,2,3-trimethylbutane, cyclohexane
90-95	1.3980	3-Methylhexane, 3-ethylpentane
95-105	1.458	Heptane, toluene, methylcyclohexane
110-118	1.4050	4-Methylheptane, 3-ethyl-2-methylpentane
118-125	1.4098	Octane, 4-methylheptane

* The principal hydrocarbons boiling within the limits indicated are given in Table 3. Hydrocarbons that occur in more than one fraction are indicated only for those fractions in which they are contained in considerable amount.

TABLE 4

Composition of the Gas Formed in the Thermal Conversion of Pentane at 450° and 500 atm.

Component	Content (vol. - %)
H_2	2.5
CH_4	65.2
C_2H_6	22.3
C_2H_4	0.1
C_3H_8	4.6
C_3H_6	0.3
ΣC_4H_{10}	1.4
Residue	3.6
	100.0

The density of the gas obtained in the various experiments was 0.79-0.81 g /liter. Thus, the gas consisted mainly of methane with very little admixture with unsaturated hydrocarbons. The gas obtained differed from the gases obtained in the thermal cracking of pentanes by being almost free from unsaturated hydrocarbons, but it was very near in composition to the gas formed by thermal alkylation of, for example, propane by means of ethylene (see above).

Conversion of Pentane in Presence of Catalysts

The conversion of pentane into liquid and gaseous hydrocarbons was studied in presence of a number of oxide catalysts—on aluminosilicate cracking catalyst, on aluminochrome and aluminomolybdenum catalysts, and on active aluminum oxide. The experimental procedure was similar to that used in the thermal conversion of pentane. Experiments were of two-hours' duration, and the amount of pentane taken in all experiments was 155 g. In order to investigate the effect of temperature on the thermocatalytic conversion of pentane, a number of experiments were carried out in presence of aluminosilicate cracking catalyst over the range 350-480°. The results obtained are given in Table 5.

TABLE 5

The Effect of Temperature on the Conversion of Pentane in Presence of an Aluminosilicate Catalyst*

Temperature (°C)	Pressure (atm.)	Amt. of catalyst (%)	Amt. of unchanged pentane (%)	Amount of conversion products (%)	
				liquid	gaseous
350	180	10.0	100.0	—	—
400	200	10.0	82.9	16.5	0.6
450	275	11.0	72.0	22.7	5.0
480	~600	21.0	32.7	21.3	46

* A fresh portion of catalyst was taken for each experiment.

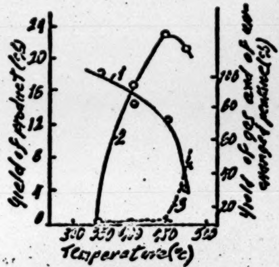

Fig. 4. Effect of temperature on the yield of conversion products of the pentane fraction at an aluminosilicate catalyst: 1) pentane, 2) liquid product, 3) gaseous product

The results given in Table 5 are presented graphically in Fig. 4. As in the case of the purely thermal conversion of pentane, the optimum conversion temperature for the conversion of pentane into higher-boiling hydrocarbons is about 450°. Further experiments were carried out at 450-460° for two hours with different catalysts. The results of this series of experiments are given in Table 6. As will be seen from the results given, the aluminosilicate

TABLE 6

Effect of Various Catalysts on the Conversion of Pentane (450°, 280 atm.)

Catalyst	Conversion of pentane (%)	Yield of products (%)			Characteristics of gasoline fraction		
		gas	Fraction, b.p.40-150°	Fraction, b.p.150-300°	n_D^{20}	d_4^{20}	Bromine number
Aluminosilicate	36.9	15.9	12.4	8.62	1.3982	0.6923	19.8
Aluminosilicate (second sample)	30.8	12.8	12.1	5.9	1.3950	0.6908	19.5
Activated aluminum oxide	39.9	16.0	15.3	8.6	1.3990	0.7023	25.3
Aluminochrome	36.0	11.7	15.4	8.9	1.4060	0.7235	23.8
Aluminomolybdenum	34.6	14.1	12.9	7.65	1.4042	0.7081	25.5
Catalyst absent	35.2	12.0	13.5	9.7	1.4087	0.7201	24.6

catalyst did not alter the experimental conditions to a significant extent, but its presence resulted in a lowering of the specific gravity of the gasoline fraction (from 0.72 to 0.69) and a rise in the total yield of low-boiling hydrocarbons in the gasoline fraction.

Aromatization catalysts (aluminochrome and aluminomolybdenum) had no essential effect on the pentane conversion process. The distillation curves for the products of thermocatalytic conversion of pentane are given in Fig. 1. The gasoline obtained by the catalytic process, as is shown by the distillation results, is considerably lighter than the product of the purely thermal process.

TABLE 7

Composition of the Gas Obtained in the Conversion of Pentane at an Aluminosilicate Catalyst.

Component	Content (vol. -%)	
	Temp. of expt. 450°	Temp. of expt. 500°
H_2	2.0	0.02
CH_4	60.6	7.8
C_2H_6	26.0	—
C_3H_6	—	0.8
C_3H_8	6.1	46.7
iso-C_4H_8	—	0.3
C_4H_8	—	1.0
iso-C_4H_{10}	1.0	21.1
n-C_4H_{10}	4.3	13.4
Residue		8.9
	100.0	100.0

TABLE 8

Hydrocarbons Detected in the Products of the Conversion of Pentane at an Aluminosilicate Catalyst

B.p. of fraction (°C)	n_D^{20}	Hydrocarbons detected
42-50	1.3875	Cyclopentane, pentane, 2,2-dimethylbutane
50-58	1.3860	Cyclopentane, 2,2- and 2,3-dimethylbutanes
58-61	1.3751	2-Methylpentane, 2,3-dimethylbutane
61-65	1.3770	2- and 3-Methylpentanes, 2,3-dimethylbutane
65-70	1.3841	Hexane, 3-methylpentane
70-85	1.3907	Methylcyclopentane, benzene, 2,2- and 2,4-dimethylpentanes, 2,3-dimethylpentane
85-91	1.3939	2- and 3-Methylhexanes, 2,3- and 3,3-dimethylpentanes
91-101	1.4005	Heptane, 3-ethylpentane, 3-methylhexane, trans-1,2-dimethylcyclopentane
101-110	1.4073	Toluene, 2,4-dimethylhexane
110-118	1.4051	2,4- and 3,4-Dimethylhexanes, toluene
118-125	1.4067	2- and 4-Methylheptanes, 1,2-dimethylcyclohexane
125-133	1.4240	Octane, m- and p-xylenes, ethylbenzene

The gas obtained in the catalytic conversion of pentane at an aluminosilicate catalyst had the composition shown in Table 7. As will be seen from these results, the gas formed at 450° consisted, as in the case of thermal conversion, mainly of methane, but the gas formed at 500° was much different in composition, the heavier hydrocarbons propane and isobutane being formed. This extremely interesting fact merits special study.

The narrow fractions of gasoline, obtained by fractionation, were qualitatively analyzed by the aid of Raman spectra. The results of the spectrum analysis are given in Table 8. Apart from the hydrocarbons indicated in this table, all the fractions contained unsaturated hydrocarbons, which was confirmed also by the value of the bromine number (19.5) for the gasoline obtained by the catalytic conversion of pentane.

From a comparison of the compositions of the gasoline of the thermal process and of that resulting from catalytic conversion of pentane, it may be stated that the gasoline obtained in the catalytic process contains a greater amount of branched hydrocarbons; also, the catalyst encourages aromatization. The formation of cycloalkanes is also very interesting. The gasoline from the catalytic process has also a somewhat higher octane number (69.2).

Thus, the investigation of the thermal and catalytic conversion of pentane under the conditions of thermal alkylation (400-500° and 300 atm.), indicates the possibility of the conversion of pentane into gas and liquid hydrocarbons, the formation of which from pentane is associated with the coupling of the reactions of cracking and alkylation, i.e., destructive alkylation, and with the polymerization process that usually accompanies the thermal alkylation reaction. The gas from the thermal conversion of pentane (which contains about 60-65% of methane) is very close in composition to the gas from thermal alkylation (which contains 50-55% of methane). The content of unsaturated hydrocarbons in the liquid products is of the same order in each case (about 15%).

The results obtained suggest that the conversion of pentane at 400-500° and 300 atm. proceeds by the reaction of thermal destructive alkylation. An aluminosilicate catalyst causes an increased yield of light products and reduced formation of unsaturated compounds.

In conclusion, it is our pleasant duty to express our thanks to A. A. Bashilov for his great assistance in the preparation of the original pentane.

SUMMARY

1. The thermocatalytic conversion of pentane at 450-460° and about 300 atm. has been investigated.

2. It has been shown that pentane, in absence of catalysts, undergoes a number of reactions, forming gaseous and liquid hydrocarbons. The composition of the mixture of hydrocarbons formed gives evidence of the occurrence of the reactions of destructive alkylation, cyclization, cracking, and polymerization.

3. It has been established that the use of certain oxide catalysts does not lead to a lowering of the reaction temperature, but affects the composition of the mixture of hydrocarbons formed; this is distinguished by the presence of a larger amount of branched hydrocarbons, and also of cycloalkanes, including cyclopentane hydrocarbons.

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CATALYTIC REACTIONS OF FIVE- AND SIX-MEMBERED CYCLOALKANES UNDER A PRESSURE OF HYDROGEN AT HIGH TEMPERATURE

N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov

The extensive study of the catalytic reactions of five- and six-membered cycloalkanes carried out by a number of investigators has resulted in the establishment of some important regularities that permit us to predict the nature of their reactions and the way in which they depend on the nature of the catalysts and reaction conditions. Thus, already in 1911 Zelinsky [1] showed that six-membered cycloalkanes are smoothly converted into the corresponding aromatic hydrocarbons at 300° in presence of platinum or palladium black.

In 1934, in a study of the aromatization of narrow fractions of Emben (Novo-bogatin) gasoline in presence of nickel-alumina catalyst, one of us, working in conjunction with Zelinsky [2], found that the catalysis products contained aromatic hydrocarbons in appreciably larger amount than that to be expected if only the dehydrogenation of six-membered cycloalkanes occurred. On the basis of these experimental results, the suggestion was then made for the first time, by these authors, that under the given conditions there occurred not only dehydrogenation of six-membered cycloalkanes, but also other reactions, which led to the formation of aromatic hydrocarbons from hydrocarbons of other classes.

In the same year, 1934, Zelinsky and Kazansky [3] showed that, under the conditions of dehydrogenation catalysis in presence of platinized charcoal, five-membered cycloalkanes react with opening of the ring and formation of alkanes. Later, Kazansky and Plate [4] found that, under the same conditions, in addition to hydrogenolysis of five-membered cycloalkanes, there occurred also the dehydrocyclization of the alkanes formed with formation of small amounts of aromatic hydrocarbons.

It must be noted that, in presence of platinized charcoal in ordinary pressure, these reactions proceed already at about 300-330°; further rise in temperature leads to appreciable destruction of the substances undergoing catalytic reaction with formation of gaseous hydrocarbons and carbonaceous deposits that rapidly deactivate the catalyst. Oxide catalysts bring about various reactions of the cycloalkanes only at temperatures above 400°. However, they then lose their activity fairly rapidly.

In this connection we considered it to be of interest to study the reactions of some individual five- and six-membered cycloalkanes in presence of a mixed oxide-metal catalyst under a high pressure of hydrogen and at a high temperature. It was considered that increase in hydrogen pressure would greatly increase the stability of the catalyst and that the simultaneous action of pressure and elevated temperature would permit deeper and more varied reactions to be effected with the original hydrocarbons.

EXPERIMENTAL

The experiments that we have carried out, in which we have studied the reactions of cyclopentane, methylcyclopentane, and cyclohexane under a pressure of 15-20 atm. of hydrogen at 460° in presence of platinized alumina, fully confirmed our suppositions. The experiments with these cycloalkanes were carried out in a specially constructed apparatus of the flow type, which permitted exact control of temperature, pressure, and rate of passage of the original hydrocarbons. The rate at which hydrogen was supplied to the reactor was measured by means of a rheometer calibrated for the pressures employed in the experiments. The temperature of the reaction zone was recorded by an autographic galvanometer. Analysis of catalyzates was carried out by separating aromatic hydrocarbons by chromatographic adsorption and subsequently fractionating both aromatic and cycloalkane-alkane parts of the catalyzate through a column having an efficiency of 70 theoretical plates. The original cycloalkanes were first distilled through the same fractionation column. Their properties are given in Table 1.

Cyclopentane

Cyclopentane (238.2 g, i.e., 320 ml) was brought into contact with the platinum-alumina catalyst at

TABLE 1

Properties of the Original Cycloalkanes

Cycloalkane	B.p. (°C at 752 mm)	n_D^{20}	d_4^{20}	MR_D Calculated	MR_D Found
Cyclopentane	49.5	1.4070	0.7445	23.09	23.17
Methylcyclopentane	71.5	1.4115	0.7496	27.71	27.88
Cyclohexane	80.8	1.4268	0.7789	27.71	27.71

TABLE 2

Fractional Composition of the Cycloalkane-Alkane Part of the Cyclopentane Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount (ml)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%) On mixture of hydrocarbons taken for fractionation	Yield (%) On original cyclopentane
1	27-29	12.0	7.4	1.3545	0.6201	14.2	10.0
2	29-38	35.5	22.2	1.3575	0.6267	42.7	34.5
3	38-52	25.5	19.0	1.4050	0.7453	36.5	22.8
4	52-73.5	3.0	2.2	1.4097	0.7480	4.2	3.0
	Residue	0.8	0.6	1.4097	—	1.1	0.5

460° and 20 atm. at a space velocity of 0.43. The liquid catalyzate (184.3 g. i.e. 258 ml; 77.4% yield) had n_D^{20} 1.3960 and d_4^{20} 0.7315. It was notable that it contained 9% by volume of aromatic hydrocarbons. The aromatic hydrocarbons (17.1 g) isolated from the catalyzate had n_D^{20} 1.4980 and d_4^{20} 0.8705; the remaining, principal part (cycloalkane-alkane) had n_D^{20} 1.3850 and d_4^{20} 0.6754. In Table 2 and Fig. 1 results are given of the precise fractionation of 52.0 g of the cycloalkane-alkane part of the catalyzate.

In the fractionation of 17.1 g of aromatic hydrocarbons from the cyclopentane catalyzate at 749.5 mm, benzene having n_D^{20} 1.5005 (14.0 g. 81.9% of total amount of aromatic hydrocarbons) was isolated; the residue (2.9 g) distilled over in the range 85-215° and had n_D^{20} 1.5380. From this residue, by distillation over sodium, a fraction (0.9 g) boiling in the range 85-160° was separated, and this was subjected to Ulmann's permanganate oxidation. From the mixture of crystalline carboxylic acids produced, the following were separated by the method of Moldavsky, Kamusher, and Kobyl'skaya [5]: benzoic acid (0.07 g; m.p. 121.6° after sublimation) and terephthalic acid (0.385 g), which was identified by conversion into its dimethyl ester (m.p. 140°).

It follows from the results cited that in the catalytic conversion of cyclopentane under the chosen conditions, the predominating reaction is the opening of the five-membered ring with formation of pentane (Fraction 2, Table 2). Simultaneously with this main reaction there occurs partial isomerization of pentane into 2-methylbutane (Fraction 1). However, special attention should be paid to the fact that appreciable amounts of methylcyclopentane (Fraction 4) and aromatic hydrocarbons, in particular benzene, toluene, and xylene, are found in the catalyzate. These new facts give convincing proof that, under the given conditions of catalytic action, cyclopentane undergoes a number of complex reactions, in which, in our opinion, an important part is played by methylene radicals, which arise as a result of the breakdown of the cyclopentane ring under the action of the platinized alumina catalyst:

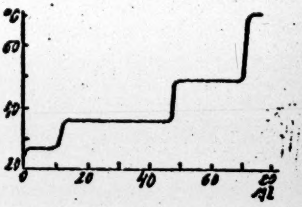
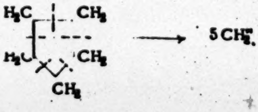


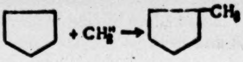
Fig. 1. Fractionation of the cycloalkane-alkane part of the cyclopentane catalyzate.



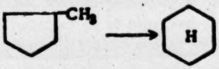
A great proportion of these transient, very reactive radicals is rapidly hydrogenated to methane:

$$CH_2^{\cdot\cdot} + H_2 \rightarrow CH_4,$$

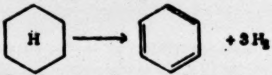
and others react with unchanged cyclopentane, causing methylation with formation of methylcyclopenane:



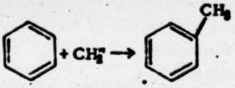
The greater part of the latter, under the given conditions, undergoes ring enlargement with formation of cyclohexane:



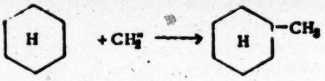
which is practically completely dehydrogenated to benzene:



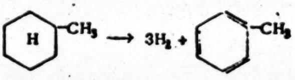
Part of the benzene formed is alkylated under the influence of the platinum-alumina catalyst (reacting similarly to cyclopentane), toluene being formed:



Further reaction gives xylene. The formation of toluene, however, may, with less probability, be represented also as the result of the alkylation of cyclohexane by methylene radicals, giving methylcyclohexane:

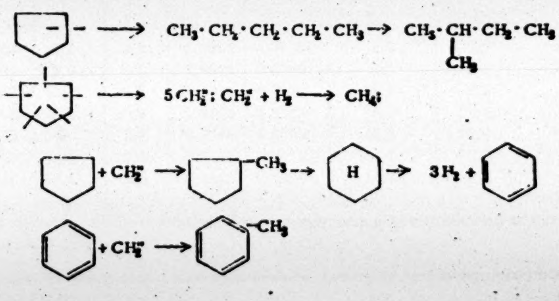


and subsequent catalytic dehydrogenation with formation of toluene:



The aromatic hydrocarbons accompanying toluene and xylene in the fraction having an upper distillation limit of 215° probably consist of a complex mixture of the products of the further methylation of benzene (polymethylbenzenes), but, owing to lack of material, this mixture of aromatic hydrocarbons was not investigated.

Thus, the complex catalytic reactions of cyclopentane under the chosen conditions may most probably be represented in the following scheme:



Analogous decomposition of cyclohexane, occurring at a nickel-alumina catalyst at 350-375° and giving methylene radicals, which alkylate benzene with formation of toluene and xylene, has already been observed by one of us and Zelinsky [6].

Methylcyclopentane

In the reaction, methylcyclopentane (374.8 g, i.e., 500 ml) was passed over the same catalyst at 460° under a pressure of hydrogen of 15 atm. and at a space velocity of 0.43. The resulting catalyzate (343.6 g, i.e. 453 ml; 91.7%) had n_D^{20} 1.4250 and d_4^{20} 0.7586; it contained 32.0% by volume of aromatic hydrocarbons. The aromatic part was separated, for investigation, from the cycloalkane and alkane parts by the chromatographic method. In Table 3 and Fig. 2 results of the analytical fractionation of the cycloalkane-alkane part of the catalyzate are given.

The cycloalkane-alkane part of the catalyzate taken for investigation (72.4 g) had n_D^{20} 1.3870 and d_4^{20} 0.7238 (Table 3). The aromatic hydrocarbons (72.1 g) separated from the methylcyclopentane catalyzate had n_D^{20} 1.4980 and d_4^{20} 0.8761. Results on the fractionation of these hydrocarbons are given in Table 4.

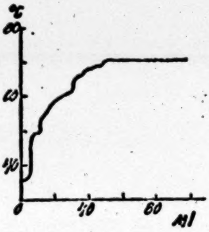
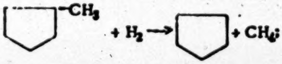


Fig. 2. Distillation curve for the cycloalkane-alkane part of the methylcyclopentane catalyzate.

As will be seen from the experimental results and from Table 4, a notable place among the products of the catalytic conversion of methylcyclopentane is occupied by aromatic hydrocarbons, among which, in addition to the predominating benzene, toluene, xylenes, and higher benzene homologs occur in small amounts.

On the basis of the results of the fractionation of the cycloalkane-alkane and aromatic parts of the methylcyclopentane catalyzate and of a comparison of the properties of the isolated fractions with the constants of individual hydrocarbons, it may be seen that in the catalytic conversion of methylcyclopentane enlargement of the five-membered ring to a six-membered ring occurs, and the latter is then completely dehydrogenated to benzene. Also, as a result of the hydrogenolysis of the methyl group of methylcyclopentane, cyclopentane is formed in appreciable amount:



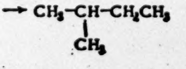
also its hydrogenolysis product, pentane:

$$+ H_2 \longrightarrow$$

$$\longrightarrow CH_3CH_2CH_2CH_2CH_3$$

and the isomerization product of the latter, 2-methylbutane:

$$CH_3CH_2CH_2CH_2CH_3 \longrightarrow$$



$$\longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3$$

Simultaneously with these reactions hydrogenolysis of the methylcyclopentane ring occurs with formation of hexane and its isomers (see Fractions 5 and 4, Table 3).

TABLE 3

Fractional Composition of the Cycloalkane-Alkane Part of the Methylcyclopentane Catalyzate.

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original methylcyclopentane
1	26 -29	2.0	1.2	1.3540	0.6205	1.7	1.3
2	29 -36	5.0	3.1	1.3580	0.6280	4.3	3.1
3	48 -55.6	10.0	7.3	1.3910	0.7327	10.1	6.2
4	55.6-62.5	15.1	10.2	1.3765	0.6735	14.1	9.4
5	62.5-69	14.0	9.5	1.3765	0.6780	13.1	8.8
6	69.0-71.5	43.0	32.2	1.4115	0.7482	44.5	27.0
	Residue	10.0	7.5	1.4115	0.7480	10.4	6.2

Thus, methylcyclopentane, like cyclopentane, undergoes various reactions under the chosen conditions, giving a complex mixture of aromatic, cycloalkane, and alkane hydrocarbons in accordance with the following scheme:

TABLE 4

Fractional Composition of the Aromatic Part of the Methylcyclopentane Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount (ml)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%) On mixture of hydrocarbons taken for fractionation	Yield (%) On original methylcyclopentane
1	to 79.5	0.5	0.4	1.4980	–	0.6	0.2
2	79.5-80.1	70.0	61.3	1.5015	0.8765	85.0	25.7
3	80.1-109.5	0.2	0.18	1.4970	–	0.2	0.1
4	109.5-110.5	2.5	2.2	1.4960	0.8670	3.0	0.9
5	126-148	2.6	2.3	1.4970	0.8650	3.2	0.9
	Residue	4.2	3.7	1.5590	–	5.1	1.5

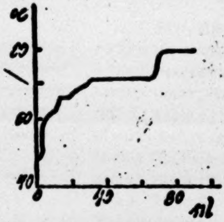
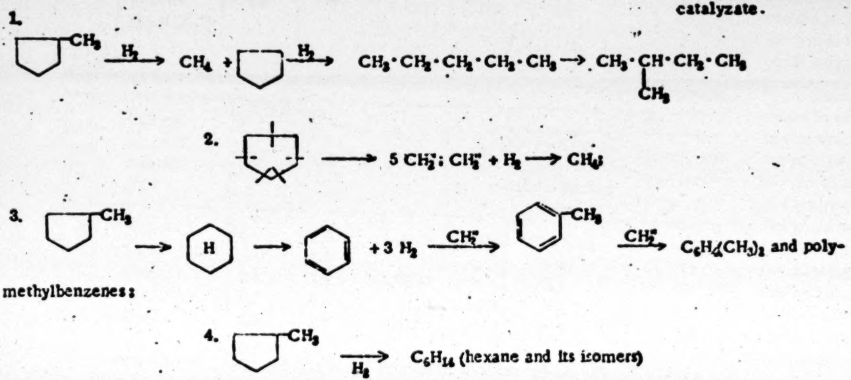


Fig. 3. Distillation curve for the cycloalkane-alkane part of the cyclohexane catalyzate.



In this case also, toluene, xylenes, and also polymethylbenzenes result from the methylation of benzene by methylene radicals formed by the "methane breakdown" of cyclopentane and also, possibly, of cyclohexane [6].

Cyclohexane

In the reaction, cyclohexane (934.7 g, i.e. 1200 ml) was treated at 460° and 15 atm. pressure of hydrogen. The catalyzate obtained (1060 ml, i.e. 873.1 g; yield 93.4%) had the following properties: n_D^{20} 1.4825, d_4^{20} 0.8237, 85% content by volume of aromatic hydrocarbons. The cycloalkane-alkane part of the catalyzate taken for investigation (107 ml, i.e. 75.9 g) had n_D^{20} 1.4165 and d_4^{20} 0.7097. The results of analytical fractionation through a column of 70 theoretical plates are given in Table 5 and Fig. 3

The aromatic hydrocarbons, separated by the chromatographic method, had n_D^{20} 1.4980 and d_4^{20} 0.8745. A part of the mixture was fractionated into narrow fractions. The results of the analytical fractionation of 60 ml (52.6 g) of aromatic hydrocarbons are given in Table 6.

As will be seen from the results given in Tables 5 and 6, the main part of the cyclohexane catalyzate, obtained under high pressure and temperature conditions, consists of aromatic hydrocarbons, comprising about 87% of benzene and small amounts of toluene, xylenes, and polyalkylbenzenes. Oxidation of Fraction 3 (110-110.5°) by permanganate, according to Ulmann, gave benzoic acid, m.p. 121.2°; and from the products of the oxidation of Fraction 4 (110.5-148°) by the same method, benzoic acid (m.p. 121°) and a mixture of benzenedicarboxylic acids (m.p. 287°) were isolated. The cycloalkane-alkane part of the catalyzate from cyclohexane contains a considerable amount (about 45%) of methylcyclopentane (Fraction 4, Table 5), some alkanes of normal and branched structure (Fraction 3, Table 5), and a comparatively small amount of unchanged cyclohexane (9.2%).

TABLE 5

Fractional Composition of the Cycloalkane-Alkane Part of the Cyclohexane Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original cyclohexane
1	28-38	4.0	2.5	1.3570	0.6258	3.3	0.5
2	38-66	20.0	13.1	1.3795	0.6537	17.3	2.6
3	66-69.5	11.0	7.3	1.3936	0.6682	9.6	1.4
4	69.5-72.0	45.0	33.7	1.4095	0.7483	44.4	6.0
5	72.0-78.9	15.0	11.3	1.4175	0.7518	14.9	2.3
	Residue (78.9-80.5)	9.0	7.0	1.4268	0.7785	9.2	1.2

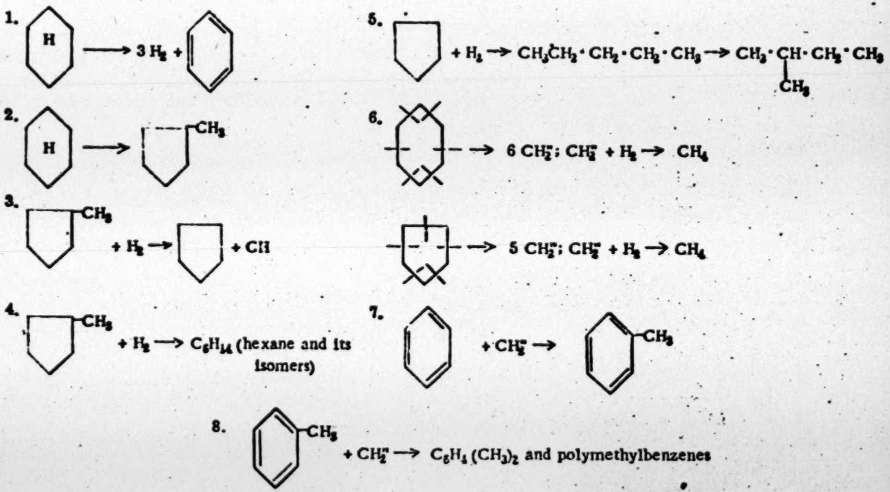
TABLE 6

Fractional Composition of the Aromatic Hydrocarbons of the Cyclohexene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original cyclohexane
1	79.5-80.1	52.0	45.6	1.5010	0.8765	87.7	71.6
2	80.1-110.0	0.15	0.1	–	–	0.2	0.1
3	110-110.5	1.0	0.9	1.4970	–	1.7	1.4
4	110.5-143	1.3	1.0	1.4960	0.8642	1.7	1.4
	Residue	3.5	3.0	1.5480	–	5.7	5.3

Also, the catalyzate contains a small amount of cyclopentane (Fraction 2, Table 5) and of other hydrocarbons having less than six carbon atoms (Fraction 1, Table 5). The results obtained form the basis of the following scheme of the various catalytic reactions of cyclohexane under the given conditions: (see below)

Thus, it has been shown in the present investigation that by the use of a comparatively low pressure of hydrogen, of elevated temperature, and of an active platinum-alumina catalyst, far-reaching changes can be brought about in five- and six-membered cycloalkanes, which have been previously considered to be comparatively inert, leading to the formation of hydrocarbons of other classes.


1.
H
→ 3 H₂ +
2.
H
CH₃
3.
CH₃
+ H₂ →
+ CH
4.
CH₃
+ H₂ → C₆H₁₄ (hexane and its isomers)
5.
+ H₂ → CH₃CH₂·CH₂·CH₂·CH₃ → CH₃·CH·CH₂·CH₃
CH₃
6.
→ 6 CH₂"; CH₂" + H₂ → CH₄
→ 5 CH₂"; CH₂" + H₂ → CH₄
7.
+ CH₂" →
CH₃
8.
CH₃
+ CH₂" → C₆H₄ (CH₃)₂ and polymethylbenzenes

SUMMARY

1. It has been found that cyclopentane, under a high pressure of hydrogen (20 atm), in presence of a platinum-alumina catalyst, and at 460°, undergoes far-reaching changes with formation not only of hydrogenolysis products (pentane, and isopentane formed by its isomerization), but also hydrogenosynthesis (methylcyclopentane, hexane and its isomers, benzene, toluene, xylene, polymethylbenzenes).

2. Under similar conditions (hydrogen pressure, 15 atm), methylcyclopentane is converted into a mixture of cyclopentane, pentane, 2-methylbutane, hexane and its isomers, benzene, toluene, xylene, and polymethylbenzenes.

3. In contact with the same catalyst at 460° under a pressure of hydrogen (15 atm), cyclohexane gives a mixture of benzene, methylcyclopentane, cyclopentane, hexanes, pentanes, toluene, xylenes, and polymethylbenzenes.

4. The synthesis reactions are in all cases to be explained by the alkylation of hydrocarbon molecules (cyclopentane, benzene, toluene) by means of methylene radicals arising under the given conditions as a result of the methane breakdown of cycloalkanes at the surface of the specific platinum-alumina catalyst.

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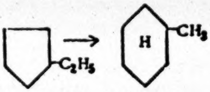
CATALYTIC ISOMERIZATION OF ETHYLCYCLOPENTANE IN THE VAPOR PHASE

N. I. Shuikin and S. S. Novikov

Study by a number of workers [1] of the isomerizing action of aluminum chloride on cyclohexane and methylcyclopentane has shown that these hydrocarbons, when heated in the liquid phase with aluminum chloride, are mutually convertible to an extent that is dependent on conditions. Subsequent investigation by Turova-Polyak and coworkers [2] has shown that not only methylcyclopentane, but also a number of other mono- and di-substituted homologs of cyclopentane are converted under definite conditions of liquid-phase catalysis with the aid of aluminum chloride into the corresponding homologs of cyclohexane. These investigations led Zelinsky, Turova-Polyak, and Gasan-Zade [3] to consider whether the isomerization of the lower homologs of cyclopentane into six-membered cycloalkanes might be applied to analytical purposes. These authors subjected dearomatized Kalin gasoline to the action of aluminum chloride and showed that the most complete isomerization of five-membered to six-membered cycles occurred at 35° in presence of 10% of aluminum chloride, the duration of treatment being 15-18 hours.

The procedure adopted in the investigations that have been carried out have generally been based on treatment of the hydrocarbons under investigation with aluminum chloride at temperatures below their boiling points, i.e., in the liquid phase. However, it would appear, and we have indeed found, that isomerization in the vapor phase is more convenient, for in this way continuous reaction with considerably less expenditure in time is assured.

In pursuance of the question of finding new methods for the catalytic synthesis of methylcyclohexane from petroleum, we have studied this reaction in the first place using pure synthetic ethylcyclopentane. We treated this hydrocarbon with a catalyst consisting of aluminum chloride deposited on activated birch charcoal, and found that at 120°, with space velocity of 0.3, isomerization of ethylcyclopentane into methylcyclohexane proceeds almost quantitatively, in spite of the equilibrium nature of this reaction:



The optimum conditions that we found for the isomerization of pure ethylcyclopentane in the vapor phase to give an enlarged ring were then employed in experiments with narrow fractions of two samples of gasoline containing ethylcyclopentane in admixture with alkanes. We took for investigation an Emben gasoline fraction of b.p. 96-105°, and a Maikop gasoline fraction of b.p. 96-102°, which had been obtained by removal of aromatics (toluene) from the 97-103° fraction of Emben and Maikop gasolines. It was natural to suppose that five-membered cycloalkanes were represented in our gasoline fractions by only ethylcyclopentane (b.p. 103.4°).

The isomerization experiments that we have carried out with these fractions, which are essentially ethylcyclopentane concentrates, have shown that from the sample of Maikop gasoline (fraction of b.p. 96-102°), it is possible to obtain about 43% of methylcyclohexane; the Emben gasoline fraction of b.p. 96-105° gave an isomerizate containing 26.5% of methylcyclohexane. Calculation shows that by making use of vapor-phase isomerization of ethylcyclopentane the content of methylcyclohexane in the 97-103° fraction of Maikop and Emben direct-distillate gasolines can be raised respectively from 35 to 60% and from 50 to 63%.

EXPERIMENTAL

We took for the experiments:

1. Pure synthetic ethylcyclopentane, b.p. 102.5-103.5°, (750 mm); n_D^{20} 1.4200 and d_4^{20} 0.7667.

2. The methylcyclohexane fraction of Maikop gasoline having the boiling range 97-103°; n_D^{20} 1.4065 and d_4^{20} 0.7389.

3. The methylcyclohexane fraction of Emben gasoline having the boiling range 97-103°, n_D^{20} 1.4173 and d_4^{20} 0.7470.

In order to free them from cyclohexane hydrocarbons, both fractions were subjected to exhaustive dehydrogenation in presence of platinized charcoal at 300°, and then to treatment with 3% oleum. The dearomatized residues so obtained had the following properties:

a) Maikop gasoline fraction: b.p. 96-102°; n_D^{20} 1.4052; d_4^{20} 0.7219.

b) Emben gasoline fraction: b.p. 96-105°; n_D^{20} 1.4015; d_4^{20} 0.7065.

The isomerization catalyst was prepared as follows: some aluminum chloride was placed on the bottom of a porcelain beaker and then covered by a layer of carefully dried activated charcoal (8-10 mm granulation; 24-hour activity to ether, 23.5); the aluminum chloride was then gradually sublimed at 140-145° (bulb of thermometer in charcoal) into the charcoal layer over a period of 40-45 minues with careful periodic stirring. The charcoal, now impregnated with aluminum chloride, was then rapidly transferred to the catalysis tube, which was hermetically sealed and was placed in an inclined electric furnace having a thermoregulator. The original material was supplied to the catalysis tube from an automatic buret, and the catalyzate was collected in a special receiver, cooled with a snow-salt mixture.

Experiment No. 1. Ethylcyclopentane (49.4 g) was passed in a stream of dry hydrogen chloride at 115-120° over the catalyst, which contained 40% of aluminum chloride, at a space velocity of 0.3. The catalyzate obtained (43.2 g), after being washed with water and dried with calcium chloride, had the following properties: b.p. 98-102°; n_D^{20} 1.4216 and d_4^{20} 0.7676. This catalyzate was then dehydrogenated over platinized charcoal at 300°, yielding a condensate that boiled in the range 98-111° and had n_D^{20} 1.4866 and d_4^{20} 0.8570. It was found to contain 92% by weight of toluene, corresponding, as calculation shows, to a 98% conversion of ethylcyclopentane into methylcyclohexane. This condensate was given two successive treatments with 3% oleum. The unabsorbed part, after being washed with water and then dried over calcium chloride, was distilled over sodium, when it boiled in the range 96-102° and had n_D^{20} 1.4162. According to its properties, this residue consisted of unchanged ethylcyclopentane mixed, evidently, with dimethylcyclopentanes, which were not separately investigated owing to lack of material.

Experiment 2. Ethylcyclopentane (30 g) was passed at 145° (other conditions being as before), over a fresh portion of the same catalyst, giving 25 g of condensate having n_D^{20} 1.4214. After dehydrogenation at 300° in contact with platinized charcoal, the catalyzate obtained had n_D^{20}. When this catalyzate was treated with 3% oleum, only 52% by volume of the hydrocarbon taken for analysis went into the acid layer. The results of this experiment show that rise in temperature to 145° greatly diminishes the extent of the isomerization of ethylcyclopentane.

In further experiments with the 96-102° fraction of Maikop gasoline freed from cyclohexane and aromatic hydrocarbons, the aluminum chloride content of the catalyst was varied. The isomerization was carried out at 120° in a stream of dry hydrogen chloride, 75 ml of gasoline being taken for each experiment. The results obtained are given in Table 1.

TABLE 1

$AlCl_3$ content of catalyst (%)	Properties of isomerizate		Properties of dehydrogenation product of isomerizate		Toluene content (% by vol.)
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	
9	1.4078	0.7297	1.4243	0.7518	30
20	1.4090	0.7310	1.4253	0.7526	33
33	1.4091	0.7313	1.4360	0.7640	42
43	1.4096	0.7320	1.4364	0.7641	43

The results given in Table 1 show that rise in the aluminum chloride content of the catalyst from 9 to 33% leads to an appreciable increase in the degree of isomerization, whereas further rise up to 43% of aluminum chloride has practically no effect on the degree of isomerization. In order to find out whether it is possible to use the catalyst repeatedly, three portions, each of 75 ml, of the same Maikop gasoline fraction were passed successively over the 43%-$AlCl_3$ catalyst, initially fresh. The results obtained are given in Table 2.

It will be seen from these results that a lowering in the activity of the catalyst becomes appreciable only after 225 ml of gasoline has been passed over it.

The subsequent experiments were carried out with the 96-105° fraction of Emben gasoline after removal of six-membered cycloalkanes and aromatic hydrocarbons; the gaseous medium in which the reaction was carried out was varied. The catalyst and other experimental conditions were the same as in preceding experiments. In order to determine the stability of the catalyst, immediately after the first portion (75 ml) of gasoline, a second portion was passed. The results of these experiments are given in Table 3.

TABLE 2

No.	Amt. of gasoline taken (ml)	Properties of isomerizate		Properties of dehydrogenation product of isomerizate		Toluene content (% by vol.)
		n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	
1	75	1.4091	0.7298	1.4368	0.7638	43
2	75	1.4067	0.7294	1.4361	0.7637	42
3	75	1.4062	0.7283	1.4235	0.7502	28

TABLE 3

Gaseous medium	Properties of isomerizate		Properties of dehydrogenation product		
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	% of aromatics
H_2	1.4040	0.7160	1.4251	0.7509	26.0
	1.4019	0.7087	1.4022	0.7110	1.0
CO_2	1.4037	0.7150	1.4244	0.7496	25.0
	1.4022	0.7090	1.4027	0.7116	2.0
N_2	1.4034	0.7160	1.4254	0.7502	26.0
	1.4022	0.7091	1.4025	–	1.5
HCl	1.4038	0.7161	1.4252	0.7561	26.5
	1.4034	0.7154	1.4248	0.7500	25.0

These results show that replacement of hydrogen chloride by H_2, CO_2, or N_2 during the first ten hours of the reaction has no significant effect on the degree of isomerization; after this period, however, in an atmosphere of hydrogen, carbon dioxide, or nitrogen, a sharp fall in the isomerizing action of the aluminum chloride occurs. On the contrary, dry hydrogen chloride definitely helps to maintain the stability of the catalyst.

SUMMARY

1. It has been shown that it is possible to bring about the isomerization of ethylcyclopentane into methylcyclohexane in the vapor phase in contact with aluminum chloride deposited in charcoal with a yield of 92% of the theoretical amount.

2. At a space velocity of 0.3, the optimum temperature for this reaction lies in the range 120-125°.

3. When the isomerization is carried out on petroleum ethylcyclopentane concentrated in the suitable gasoline fraction, the nature of the latter has no significant effect on the course of the isomerization.

4. On the basis of this observation, a method has been found for the catalytic synthesis of methylcyclohexane from petroleum ethylcyclopentane.

5. Dry hydrogen chloride aids in the maintenance of the isomerizing propensity of aluminum chloride deposited on activated charcoal.

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ADDITION REACTIONS OF FLUOROALKENES

COMMUNICATION 2. ADDITION OF ALCOHOLS AND THIOLS TO PERFLUOROPROPENE

I.L. Knunyants, A.I. Shchekotikhin, and A.V. Fokin

As previously shown, perfluoroalkenes readily undergo addition with nucleophilic reagents in presence of alkalis [1]. The question of the direction of the addition of these substances to perfluoropropene and other perfluoroalkenes has not been considered, because the perfluoro hydrocarbon C_3F_6, obtained by pyrolysis of polytetrafluoroethylene, has until recently, been assigned the structure of perfluorocyclopropane [2].

The interaction of the perfluoro hydrocarbon C_3F_6 with hydrogen fluoride and hydrogen bromide has been regarded only from the point of view of a proven cyclopropane structure [3], the structure of the addition products remaining unestablished. Recently, however, study of the infrared spectra of C_3F_6 has shown that it contains a double bond, and in this connection the question arose of the determination of the structures of the addition products formed with various reagents. The solution of this problem as well as the final chemical proof of the structure of the perfluoro hydrocarbon C_3F_6 was also of real theoretical interest.

The trifluoromethyl group has a powerful electron-attracting effect, shown, for example, by the fact that it is 100% meta-directing. Its presence in the molecule of perfluoropropene is bound to have an effect on the polarization of this compound and therefore on the direction of addition of hydrogen-containing substances, in accordance with the electronic basis of Markovnikov's rule:

$$F_3C \curvearrowright CF \curvearrowright\!\!=CF_2.$$

According to this, the proton of the attacking reagent should add to the middle carbon atom (contrary to propene). Experiment has supported this supposition.

With a view to the more ready identification of the addition products, the smooth reactions of perfluoroalkenes with alcohols and thiols were chosen for study. As was expected, alcohols readily react with perfluoropropene in presence of alkalis with formation of alkyl 2H-hexafluoropropyl ethers:

$$CF_3-CF=CF_2 + HOR \rightarrow CF_3-CFH-CF_2-O-R.$$

Thiols react in a similar way with formation of alkyl 2H-hexafluoropropyl sulfides:

$$CF_3-CF=CF_2 + HSR \rightarrow CF_3-CFH-CF_2-S-R.$$

As a result of the addition to perfluoropropene of methyl, ethyl, propyl, isopropyl, and butyl alcohols and of phenol, there were obtained in good yields the corresponding methyl, ethyl, propyl, isopropyl, butyl, and phenyl 2H-hexafluoropropyl ethers.

The properties of these compounds are given in Table 1.

TABLE 1
Properties of Alkyl 2H-Hexafluoropropyl Ethers

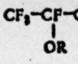
No.	Formula	B.p. at norm. press. (°C)	Specific gravity	Refractive index
1	$CF_3-CFH-CF_2-O-CH_3$	54-55	1.429/10°	1.2850/10°
2	$CF_3-CFH-CF_2-O-C_2H_5$	64-65	1.299/20°	1.2960/20°
3	$CF_3-CFH-CF_2-O-(CH_2)_2-CH_3$	92-93	1.260/20°	1.3110/20°
4	$CF_3-CFH-CF_2-O-C_3H_7i$	76	1.280/22°	1.3220/22°
5	$CF_3-CFH-CF_2-O-(CH_2)_3-CH_3$	108	1.260/27°	1.3390/27°
6	$CF_3-CFH-CF_2-O-C_6H_5$	95 at 95 mm	1.371/20°	1.3965/20°

Addition to perfluoropropene of methanethiol, ethanethiol, and 2-mercaptoethanol yielded the corresponding sulfides: methyl, ethyl, and 2-hydroxyethyl 2H-hexafluoropropyl sulfides, the properties of which are given in Table 2.

The direction of addition and the structures of the compounds obtained were determined by the following considerations, which were confirmed by the facts. Addition of alcohols to perfluoropropene can theoretically lead to compounds of two types, I and II:

$$CF_3-CFH-CF_2-OR;$$

(I)



$$CF_3-\underset{OR}{CF}-CF_2H.$$

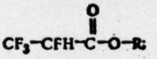
(II)

TABLE 2

Properties of Alkyl 2H-Hexafluoropropyl Sulfides

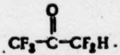
No.	Formula	B.p. at norm. press. (°C)	Specific gravity at 20°	Refractive index at 20°
1	$CF_3-CFH-CF_2-S-CH_3$	87	1.380	1.3443
2	$CF_3-CFH-CF_2-S-C_2H_5$	101	1.322	1.3548
3	$CF_3-CFH-CF_2-S-CH_2-CH_2OH$	54 at 5 mm	1.546	1.3835

When these compounds are hydrolyzed there should be formed: esters of 2H-tetrafluoropropionic acid (III) from compounds of the first type, and pentafluoroacetone (IV) from those of the second type:



$$CF_3-CFH-\overset{O}{\overset{\|}{C}}-O-R;$$

(III)

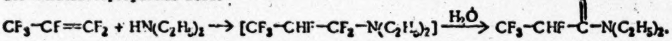


$$CF_3-\overset{O}{\overset{\|}{C}}-CF_2H.$$

(IV)

Hydrolysis of the products of addition of alcohols to perfluoropropene, brought about by concentrated sulfuric acid in presence of SiO_2, which binds hydrogen fluoride, leads exclusively to the formation of esters of 2H-tetrafluoropropionic acid (III). Thus, hydrolysis of 2H-hexafluoropropyl methyl ether and of ethyl 2H-hexafluoropropyl ether yielded respectively the methyl and ethyl esters of 2H-tetrafluoropropionic acid as sole reaction products.

In order to prove the direction of addition of hydrogen-containing substances to perfluoropropene, use was made also of the reaction of fluoroalkenes with alkylamines. Diethylamine, in adding to perfluoropropene, gave what was evidently an unstable amine, which was converted by water into the diethylamide of 2H-tetrafluoropropionic acid:



$$CF_3-CF{=\!=}CF_2 + HN(C_2H_5)_2 \longrightarrow [CF_3-CHF-CF_2-N(C_2H_5)_2] \xrightarrow{H_2O} CF_3-CHF-\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2.$$

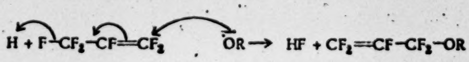
Both the structure of perfluoropropene and the direction of addition to this compound of various hydrogen-containing substances are proved by the fact that these substances are obtained.

In the course of our study of the addition of alcohols to perfluoropropene it was shown that, in addition to alkyl 2H-hexafluoropropyl ethers, small amounts of unsaturated compounds were formed, which were readily separated from other reaction products in the form of dibromides. Analysis of the dibromides showed that they were products of the addition of bromine to alkyl perfluoroallyl ethers formed together with alkyl 2H-hexafluoropropyl ethers during the addition of alcohols to perfluoropropene. It was natural to consider that the alkyl perfluoroallyl ethers (II) arose from the alkyl 2H-hexafluoropropyl ethers (I) by the splitting from the latter of hydrogen fluoride under the action of the alkalis catalyzing the reaction:

$$\underset{(I)}{CF_3-CFH-CF_2-OR} \xrightarrow{-HF} \underset{(II)}{CF_2{=\!=}CF-CF_2-OR}.$$

However, negative results obtained in specially designed experiments aiming at the splitting of hydrogen fluoride from alkyl 2H-hexafluoropropyl ethers by the aid of quinoline, alkoxides, alkalies, or potassium fluoride, even under very severe conditions (200°), compelled us to reject the hypothesis. In all cases the original ether remained unchanged, although formation of alkyl perfluoroallyl ethers proceeds during the addition of an alcohol to perfluoropropene at a temperature of only 50-60°. Another possible explanation of the formation of alkyl perfluoroallyl ethers is the direct replacement of one of the fluorine atoms in the trifluomethyl group by alkoxyl. This explanation, however, is in conflict with the known facts concerning the stability of fluorine in the trifluoromethyl group and with the well known properties of fluoroalkenes.

In the previous communication [1], it was suggested, on the basis of the chemical properties of perfluoroalkenes, that the primary process, determining addition reactions to perfluoroalkenes due to electron depletion of the π-bond of the perfluoroalkene, is an anionoid attack by a nucleophilic reagent, which donates electrons to carbon atoms united by a double bond. The polarizability in the moment of reaction increases the σ,π-conjugation and makes a fluorene atom of the trifluoromethyl group mobile, so that it comes away as an anion:



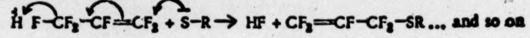
$$H + F-CF_2-CF{=\!=}CF_2 \quad \bar{O}R \longrightarrow HF + CF_2{=\!=}CF-CF_2-OR$$

These reaction result in the formation of alkyl perfluoroallyl ethers.

In a similar way, in the addition of thiols to perfluoropropene, there are formed, not only the usual addition products, but also disulfides of the following structure:

$$CH_3-S-CF_2-CFH-CF_2-S-CH_3.$$

The formation of these substances is the result of the further addition of thiols to alkyl perfluoroallyl sulfides formed similarly to the alkyl perfluoroallyl ethers:



$$\overset{+}{H}\ F-CF_2-CF=CF_2 + \overset{-}{S}-R \rightarrow HF + CF_2=CF-CF_2-SR \ldots \text{ and so on}$$

$$CF_2=CF-CF_2-S\cdot R + HS\cdot R \rightarrow R\cdot S-CF_2-CFH-CF_2-SR$$

The formation of disulfides of this type is a further proof of the correctness of hypotheses advanced, but the question of the mechanism of the formation of alkyl perfluoroallyl ethers and sulfides may be solved finally by a study of the addition of alcohols and thiols to perfluoropropene having labeled carbon atoms.

EXPERIMENTAL

I. Reaction of Alcohols with Perfluoropropene

1. 2H-Hexafluoropropyl methyl ether. Freshly distilled methanol (3.0 g), powdered, fused caustic potash (0.7 g), and condensed perfluoropropene (15 g), were introduced into a 100-cc autoclave of chromium-nickel stainless steel cooled to −70°. The autoclave was maintained at 60° for 13 hours with constant rotation, and was then cooled to −70°. Unchanged perfluoropropene (0.4 liter, i.e. 2.6 g) was driven off, and a liquid distillate (16.4 g) then came over at 44-53°. The crude ether was brominated by the method described in the next section, and a fraction was then obtained having a b.p. of 52-55° (14.2 g, 83% of perfluoropropene taken for reaction). Redistillation yielded a substance of b.p. 54-55°, which appeared to be pure 2H-hexafluoropropyl methyl ether. It was a colorless mobile liquid of pleasant odor: d_4^{19} 1.429; n_D^{19} 1.2850; calculated MR 23.09; found MR 22.30.

Found %: F 62.4; M 176 (cryoscopic)

$C_4H_4OF_6$. Calculated %: F 62.6; M 182

2. 2,3-Dibromopentafluoropropyl methyl ether. The fraction of b.p. 44-53° (15.7 g), the mixture of saturated and unsaturated ethers obtained by the method described in the first section, was placed in a test tube cooled with ice water and provided with reflux condenser and with a buret, from which bromine was slowly added. When decolorization ceased, a further amount of bromine was added, the reaction mixture was set aside for thirty minutes at room temperature, and it was then washed with saturated thiosulfate solution and with water. The product was dried over anhydrous magnesium sulfate and was fractionated (17 g). The following fractions were separated:

Fraction I, b.p. 52- 55°; 14.2 g
Fraction II, b.p. 128-136°; 1.5 g

Fraction II, b.p. 128-136°, boiled after redistillation at 136° (2,3-dibromopentafluoropropyl methyl ether). This compound is a colorless liquid having a terpenelike odor: d_4^{20} 1.900; n_D^{20} 1.3700; found MR 38.40; calculated MR 37.65.

Found %: Br 48.6

$C_4H_3OF_5Br_2$. Calculated %: Br 49.8

3. Ethyl 2H-hexafluoropropyl ether. Absolute ethanol (3.0 g), powdered fused caustic potash (0.8 g), and perfluoropropene (13.4 g, i.e. 37% excess) were introduced into a 100-cc autoclave of chromium-nickel stainless steel cooled to −70°. The autoclave was maintained at 50-60° for 14 hours with constant rotation, and was then cooled to −60-70°. Unchanged perfluoropropene (0.7 liter, i.e. 4.55 g), was driven off, and a liquid distillate (11.0 g, 92.7% of perfluoropropene taken for reaction), then came over at 57-65°. After treatment with bromine in the usual way (see Section 2), the crude product (12.9 g) was fractionated, the 64-65° fraction, i.e., ethyl 2H-hexafluoropropyl ether (9.4 g, 79.3%), being collected. It was a clear mobile liquid of pleasant odor; d_4^{20} 1.299; n_D^{20} 1.2960; found MR 27.90; calculated MR 27.71.

Found %: F 57.6; M 190 (cryoscopic)

$C_5H_6OF_6$. Calculated %: F 58.2; M 196

4. 2H-Hexafluoropropyl propyl ether. Freshly distilled propyl alcohol (11.6 g), powdered fused caustic potash (0.9 g), and condensed perfluoropropene (8.4 g) were introduced into a 100-cc autoclave. The autoclave was heated at 55-60° with constant rotation for 16 hours, and was then cooled to −70°. Unchanged perfluoropropene was driven off (0.2 liter, i.e. 1.3 g). Fractionation of the residue yielded:

Fraction I,	b.p. 75-89°;	6.5 g.
Fraction II,	b.p. 89-98°;	4.0 g.
Residue		4.5 g.

Fraction II (mainly alcohol), was washed several times with water and then dried over anhydrous magnesium sulfate, thus giving a further 1.9 g of product, which was added to Fraction I. The crude ether was treated with bromine by the method described in Section 2, and the saturated propyl ether was distilled from the dibromo compound at 90-93°, yielding practically pure 2H-hexafluoropropyl propyl ether (6.1 g), b.p. 92-93°. It was a clear, colorless mobile liquid of pleasant odor: d_4^{20} 1.260; n_D^{20} 1.3110; found MR 32.0; calculated MR 32.30.

Found %: F 54.4
$C_6H_8OF_6$. Calculated %: F 54.3

5. 2H-Hexafluoropropyl isopropyl ether. Freshly distilled isopropyl alcohol (10.7 g), powdered fused caustic potash (0.7 g), and perfluoropropene (32.6 g, 20% excess) were introduced into an autoclave cooled to −70°. The autoclave was heated to 55-60° with constant rotation for 20 hours, and was then cooled to −70°. Unchanged perfluoropropene was driven off (2.69 liter, i.e. 17.6 g). Fractionation of the remainder (16 g), gave the following fractions:

Fraction I,	b.p. 65-75°,	6.5 g.
Fraction II,	b.p. 75-84°,	6.5 g.
Residue		2.8 g.

Fraction II was washed several times with cold water and was dried over anhydrous magnesium sulfate, yielding a further 2.3 g of product, which was added to Fraction I. Refractionation yielded a fraction of b.p. 65-76° (8.5 g, 40.5%). This fraction was treated with bromine in the usual way (see Section 2). The saturated 2H-hexafluoropropyl isopropyl ether was distilled from the dibromo compound at 76° (3.6 g, 17.1%). It was a clear, colorless, mobile liquid of pleasant odor: b.p. 76°; d_4^{22} 1.280; n_D^{22} 1.3220; found MR 31.83; calculated MR 32.50.

Found %: F 53.2.
$C_6H_8OF_6$. Calculated %: F 54.3.

6. Butyl 2H-hexafluoropropyl ether. Freshly distilled butyl alcohol (12.8 g), powdered fused caustic potash (1.4 g), and condensed perfluoropropene (12 g) were introduced into a autoclave cooled to −70°. The autoclave was heated at 55-60°, with constant rotation for 18 hours, and then cooled to −70°. The autoclave was opened, and unchanged perfluoropropene was driven off (0.74 liter, i.e. 4.9 g), and a liquid condensate (19.9 g) was also obtained. Fractionation of the latter yielded:

Fraction I,	b.p. 82-90°,	1 g
Fraction II,	b.p. 105-110°,	10.1 g.
Fraction III,	b.p. 110-118°,	5.7 g.
Residue		3.1 g

Fraction II (b.p. 105-110°) was boiled in a flask under reflux in presence of sodium, in order to remove alcohol; it was then fractionated, the 105-109° fraction being collected. After bromination, the saturated butyl 2H-hexafluoropropyl ether was distilled from the dibromo compound at 108° (3.6 g, 34%). It was a colorless, mobile liquid of pleasant odor: b.p. 108°; d_4^{27} 1.270; n_D^{27} 1.3390; found MR 36.90; calculated MR 37.05.

Found %: F 49.3.
$C_7H_{10}OF_6$. Calculated %: F 50.9

7. 2H-Hexafluoropropyl phenyl ether. Freshly distilled phenol (10.8), powdered fused caustic potash (0.7 g), and liquid perfluoropropene (13.3 g) were introduced into an autoclave cooled to −70°. The autoclave was hermetically sealed and heated at 50°, with constant rotation for 10 hours, and was then cooled to −70°. Unchanged perfluoropropene (0.24 liter, i.e. 1.6 g), was driven off, and the reaction mixture (22 g) was washed

with 10% caustic alkali to remove unchanged phenol. It was then extracted with ether, and the ether solution was washed with water and dried over calcium chloride. The ether was removed, and the residue was vacuum-fractionated. The main fraction boiled at 92-94°/93 mm. Redistillation yielded practically pure 2H-hexafluoropropyl phenyl ether. b.p. 95°/95 mm (44.7% yield). It was a clear, colorless liquid of pleasant odor: d_4^{18} 1.371; n_D^{20} 1.3965; found MR 42.60; calculated MR 42.58.

Found %: F 45.9.
$C_9H_6F_6O$. Calculated %: F 46.8.

II. Hydrolysis of Alkyl 2H-Hexafluoropropyl Ethers into Alkyl Esters of 2H-Tetrafluoropropionic Acid

8. Methyl 2H-tetrafluoropropionate. Sulfuric acid of sp. gr. 1.84 (10 g), and 11.8 g 2H-hexafluoropropyl methyl ether of b.p. 52-55°, were introduced into an autoclave of chromium-nickel stainless steel cooled in a mixture of ice and common salt. Powdered glass (2.2 g), was added for binding hydrogen fluoride. The autoclave was hermetically closed and was heated at 60-65° with constant rotation for three hours.

The autoclave was then cooled, and the reaction mixture was carefully poured into ice water, when layers were formed. The lower, ester layer, which had a yellowish color, was separated, washed with a saturated solution of bicarbonate and then water and dried over freshly roasted magnesium sulfate. The aqueous layer was extracted with ether, and the ether extract was dried over magnesium sulfate. The ether was removed and the main product was added to the residue in the distilling flask. Distillation yielded methyl 2H-tetrafluoropropionate (6.9 g, 65.6%), a colorless liquid having a characteristic odor: b.p. 96°; d_4^{20} 1.353; n_D^{20} 1.3192; found MR 23.27; calculated MR 22.73.

Found %: F 46.3; M 157 (cryoscopic).
$C_4H_4O_2F_4$. Calculated %: F 47.5; M 160.

9. Ethyl 2H-tetrafluoropropionate. Sulfuric acid of sp. gr. 1.84 (10 g), ethyl 2H-hexafluoropropyl ether of b.p. 64-65° (15.0 g), and powdered glass for binding hydrogen fluoride (2.3 g), were introduced into an autoclave cooled by a mixture of ice and common salt. The autoclave was heated at 75°, with constant rotation for three hours, and was then cooled. The reaction mixture was carefully poured into ice water, when layers were formed. The lower layer was separated, washed with a saturated solution of bicarbonate and with water, and dried over freshly roasted magnesium sulfate. The aqueous layer was extraced with ether, and the ether extract was dried over magnesium sulfate. The main product was added to the residue remaining in the distillation flask after removal of ether, and fractionation yielded ethyl 2H-tetrafluoropropionate (7.9 g, 59.4%), a colorless, mobile liquid of characteristic odor: b.p. 108-109°; d_4^{20} 1.289; n_D^{20} 1.3260; found MR 27.19; calculated MR 26.86.

Found %: F 42.8; M 169 (cryoscopic).
$C_5H_6O_2F_4$. Calculated %: F 43.7; M 174.

III. Addition of Thiols to Perfluoropropene

10. 2H-Hexafluoropropyl methyl sulfide. Methanethiol (10.5 g), perfluoropropene (33 g), and dry caustic soda (1 g), were introduced into a 70-cc steel autoclave. The autoclave was heated for six hours at 120-140°. It was then cooled, and unchanged perfluoropropene was driven off (2 liters). A liquid product was extracted from the autoclave (12 ml) and was fractionated; refractionation yielded:

Fraction I, b.p. 85-87° 7.5 g;
Fraction II, b.p. 72°/32 mm, 2 g.

2H-hexafluoropropyl methyl sulfide is a clear, colorless liquid, having a sharp, unpleasant odor: d_4^{20} 1.380; n_D^{20} 1.3443; found MR 30.40; calculated MR 29.37. b.p. 87°.

Found %: S 15.80; F 55.3.
$C_4H_4SF_6$. Calculated %: S 16.10; F 57.50

11. Ethyl 2H-hexafluoropropyl sulfide. Ethanethiol (12.5 g), perfluoropropene (30 g), and dry caustic soda (1 g) were introduced into a 70-cc autoclave. The autoclave was heated for six hours at 120-140° with constant rotation. It was then cooled, and unchanged perfluoropropene was driven off (2 liters). The crude product (21 g) was fractionated. Refractionation yielded the fractions:

Fraction I, b.p. 100-102°/752 mm, 17 g (34%);
Fraction II, b.p. 50-52°/100 mm, 3.5 g.

After redistillation, Fraction I boiled at 100-101°.

Ethyl 2H-hexafluoropropyl sulfide is a clear, colorless liquid of unpleasant odor: d_4^{20} 1.322; n_D^{20} 1.3548; found MR 34.93; calculated MR 33.991.

Found %: S 14.30; F 49.22.
$C_5H_6SF_6$. Calculated %: S 15.10; F 53.80.

Refractionation of Fraction II yielded as main product a liquid of b.p. 89-90°/140 mm, which appeared to be practically pure disulfide. It was a clear, yellow liquid having a specific odor: b.p. 89-90°/140 mm: d_4^{20} 1.294; n_D^{20} 1.4045. Found MR 49.03; calculated MR 50.56.

Found %: S 24.80; F 38.1.
$C_4F_5S_2H$. Calculated %: S 25.30; F 37.6

12. 2H-Hexafluoropropyl 2-hydroxyethyl sulfide. 2-Mercaptoethanol (10 g), perfluoropropene (20 g), and dry caustic soda (0.8 g) were introduced into a steel cylinder, 70 cc in volume. The hermetically closed cylinder was heated for six hours at 100-120° and then cooled. It was then opened, and unchanged perfluoropropene was driven off. The crude product was washed with alkali and extracted with ether. The ether extract was dried overnight with magnesium sulfate, the ether was driven off, and the residue was vacuum-fractionated, a fraction of b.p. 53-54°/5 mm being separated. It was 2H-hexafluoropropyl 2-hydroxyethyl sulfide (6 g, 20.5%), a clear, colorless liquid of pleasant odor; it has d_4^{20} 1.546; n_D^{20} 1.3835; found MR 34.5; calculated MR 35.51.

Found %: S 14.60.
$C_5H_6OSF_6$. Calculated %: S 14.05

13. Addition of diethylamine to perfluoropropene. Diethylamine (10 g), perfluoropropene (20 g), and borax (1 g) were introduced into a 70-cc stainless-steel cylinder. The hermetically sealed cylinder was heated for four hours at 90°, and the cylinder was then cooled to −70°. Unchanged perfluoropropene was driven off, and the residual liquid was washed with water, extracted with ether, and dried with magnesium sulfate. The product was then vacuum-fractionated, the fraction of b.p. 89°/22 mm, the diethylamide of 2H-tetrafluoropropionic acid, being separated. It was a clear, colorless liquid of unpleasant odor: d_4^{20} 1.228; n_D^{20} 1.3910; found MR 38.92; calculated MR 38.39.

Found %: F 38.8; N 6.80
$C_7H_{11}F_4ON$. Calculated %: F 37.9; N 6.95

SUMMARY

1. Perfluoropropene, in presence of alkalis, readily unites with alcohols and thiols, and the hydrogen atom of the hydroxyl group of the alcohol or of the mercapto group of the thiol, in contrast to its behavior, in the case of propene, adds to the middle carbon atom of perfluoropropene.

2. The alkyl 2H-hexafluoropropyl ethers formed as a result of reaction of perfluoropropene with alcohols are readily hydrolyzed into esters of 2H-tetrafluoropropionic acid (proof of direction of addition).

3. The normal addition reaction, leading to formation of alkyl 2H-hexafluoropropyl ethers, is accompanied by the formation in appreciable amount of alkyl perfluoroallyl ethers (or alkyl perfluoroallyl sulfides in the case of reaction with thiols).

4. It has been established that the fluorine atoms of the trifluoromethyl group of perfluoropropene, unlike those in compounds carrying a trifluoromethyl group on an atom not linked to a neighbor by a multiple bond, have an appreciable degree of mobility.

5. The formation of perfluoroallyl derivatives in reactions of perfluoropropene with substances containing mobile hydrogen atoms (alcohols, thiols, etc.) cannot be regarded as a direct replacement of a fluorine atom of the trifluoromethyl group (by alkoxyl or alkylthio), but is the result of anionoid attack by a nucleophilic reagent on the extreme carbon atom of perfluoropropene having the least electron density: in the moment of attack, transposition of the double bond occurs, and one of the fluorine atoms of the trifluoromethyl group is removed as an anion.

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CRYSTALLINE ORGANOLITHIUM COMPOUNDS. BENZYLLITHIUM

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Benzyllithium, being the simplest aralkyl organolithium compound, is of considerable interest: its properties differ from those of the aliphatic and aromatic compounds in the direction of increased reactivity (which is made use of mainly for analytical purposes) [1]. It is probable that this increased reactivity also explains why there have been no satisfactory methods up to the present for the preparation of benzyllithium in a pure form, either in solution, or in the isolated, solid (crystalline) state. Actually, the usual methods for the synthesis or organolithium compounds are of little applicability in this case.

Thus, when benzyl halide is treated directly with lithium, the reaction does not stop at the organolithium-compound stage, because a further condensation reaction with benzyl halide rapidly sets in with formation of dibenzyl [2]:

$$C_6H_5CH_2X + 2Li \rightarrow C_6H_5CH_2Li + LiX; \quad C_6H_5CH_2X + C_6H_5CH_2Li \rightarrow LiX + C_6H_5CH_2CH_2C_6H_5.$$

The double-decomposition reaction between organolithium compounds and benzyl halides is more complex than this:

$$nC_4H_9Li + C_6H_5CH_2Cl \rightarrow nC_8H_{18} + C_6H_5CH_2C_4H_9 + C_6H_5CH_2CH_2C_6H_5.$$

These condensations proceed so readily that it is possible to demonstrate the intermediate formation of benzyllithium only indirectly: reaction of benzyl chloride with butyllithium at −50° followed by carboxylation with solid carbon dioxide gives a small amount of phenylacetic acid [3]:

$$C_6H_5CH_2Cl + nC_4H_9Li \rightarrow C_6H_5CH_2Li + nC_4H_9Cl \xrightarrow{CO_2} C_6H_5CH_2COOLi.$$

The double-decomposition reactions between organomagnesium compounds and lithium or RLi are of considerable interest:

$$C_6H_5CH_2MgCl + 2Li \rightarrow C_6H_5CH_2Li + LiCl + Mg \qquad (1)$$

$$C_6H_5CH_2MgCl + 2C_6H_5Li \rightarrow C_6H_5CH_2Li + (C_6H_5)_2Mg + LiCl \qquad (2)$$

However, both of these reactions, apart from the fact that they proceed extremely slowly and do not give consistently reproducible results, always yield a mixture of benzyllithium, organomagnesium compound, and lithium salt [4].

Finally, experiments have been described on the isolation of benzyllithium by means of the double-decomposition reaction between dibenzylmercury and ethyllithium:

$$(C_6H_5CH_2)_2Hg + 2C_2H_5Li \rightarrow 2C_6H_5CH_2Li + (C_2H_5)_2Hg.$$

This method also has great drawbacks and could not be applied as a convenient synthesis of benzyllithium. There were difficulties in the preparation of large amounts of the starting materials, both of pure dibenzylmercury, and also of ethyllithium; for, until recently, this was synthesized from diethylmercury and lithium. A further drawback was the formation in this reaction of the highly toxic diethylmercury.

The authors who described this method could not obtain sufficient quantities of benzyllithium, and also, evidently, did not obtain a completely pure product, for it was greasy and did not come away from the walls. The benzyllithium was analyzed by decomposing the whole amount by alcohol in a filtration apparatus; the yield of benzyllithium was not indicated [5].

As indicated in a previous communication [6], we have developed a convenient method for the preparation of pure crystalline ethyllithium by the reaction of ethyl bromide (or chloride) with lithium, so avoiding the highly toxic mercury compounds that were used previously. This enabled us to make a closer investigation of the double-decomposition reactions of ethyllithium with organometallic compounds of other metals, in particular antimony [7]. This procedure has been applied also to the synthesis of benzyllithium:

$$(C_6H_5CH)_3\,Sb + 3C_2H_5Li \rightarrow 3C_6H_5CH_2Li + (C_2H_5)_3Sb.$$

The preparation of pure benzyllithium presents certain experimental difficulties owing to its low stability and high reactivity. It is necessary to work with pure starting materials (tribenzylantimony, ethyllithium), in dry solvents (pentane, thiophene-free benzene), in an atmosphere of pure dry nitrogen, and in special apparatus permitting isolation from moisture and atmospheric oxygen [7].

It is of interest to note that at reaction temperatures of above 40° the color of solution and precipitate changes considerably, becoming orange and then, with further rise in temperature, brownish red. A similar change has been observed previously by Hein and coworkers [5] and was erroneously attributed to the formation of "reddish-violet lithium compounds of the same type as disodiumstilbene $C_6H_5CHNa-CHNaC_6H_5$". When the reaction was carried out at 65-75° with an excess of ethyllithium, we isolated, in quantitative yield, a brownish-red crystalline compound corresponding accurately in analysis to the formula $C_7H_6Li_2$. A compound of the type $C_6H_5CHLi-CHLiC_6H_5$ would contain half as much lithium.

Tribenzylantimony, in the form of a snow-white, finely crystalline powder, was prepared under nitrogen in an apparatus having ground joints by the action of antimony trichloride on benzylmagnesium chloride. The method for the preparation of tribenzylantimony described by Tsukervanik and Smirnov [8], in which apparatus similar to that used in the synthesis of tribenzylarsenic [9] is used, is less convenient.

EXPERIMENTAL

Preparation of Tribenzylantimony. The preparation of an ether solution of benzylmagnesium chloride was carried out in a one-liter three-necked flask attached by ground joints to reflux condenser, dropping funnel, stirrer with mercury seal, and source of pure dry nitrogen. The condenser was connected to a Tishchenko vessel containing concentrated sulfuric acid. Iodine-activated magnesium (8.1 g, i.e. 0.33 g-atom) and absolute ether (200 ml) were introduced into the nitrogen-filled flask. Some benzyl chloride (about 5 ml) was added to initiate the reaction, and the remaining amount was diluted with 100 ml of absolute ether and added gradually so as to maintain a vigorous boil, about 35 minutes being required (total amount added, 42.4 g, i.e. 0.33 mole). Boiling was continued for a further 15 minutes, and the flask was then cooled with ice (the nitrogen stream being maintained).

Then, with cooling and good stirring, a solution was added of antimony trichloride (22.8 g; 0.1 mole) in absolute ether (100 ml) over a period of 10-15 minutes. When the addition was complete, the contents of the flask consisted of a fairly thick light-gray mass. While nitrogen continued to pass, the flask was rapidly disconnected from the stirrer and closed with a stopper; the condenser was removed and the reaction mixture was poured, while nitrogen continued to pass, into a large, closed funnel of 0.75 liter capacity for filtration under nitrogen through a porous glass filter. The funnel and receiver for the filtrate had been carefully dried previously and were full of nitrogen. The funnel was closed, and filtration proceeded under a pressure of nitrogen. Precipitate remaining on the walls of the flask was washed off with a small amount of absolute ether and was also rapidly transferred to the filter. The precipitate on the filter was washed four times with absolute ether (50-ml portions); the filtrate, which was somewhat turbid, was left under nitrogen until the next day. It was then filtered under nitrogen through a dry, folded filter paper into a two-necked nitrogen tube connected with condenser and receiver filled with nitrogen. Ether was then distilled off under nitrogen until the volume was about 40 ml. The nitrogen tube was disconnected from the condenser and cooled to room temperature, while nitrogen continued to pass; pentane (30 ml) was then added, and the mixture was cooled with ice. The fine snow-white crystals that appeared were filtered off under a pressure of nitrogen, washed three times with pentane, dried in a stream of nitrogen, and sealed in ampoules. The yield was 50-55%. The melting point of tribenzylantimony was determined in a capillary tube sealed under nitrogen. The value found was 87°, the value given in the literature being 85-90° [8].

For analysis [10] the substance was sealed in ampoules under nitrogen in amounts of about 0.2-0.4 g. An ampoule was weighed, opened, and reweighed rapidly after substance had been poured out into a Kjeldahl flask.

Found %: Sb 31.14; 30.71
$C_{21}H_{21}Sb$. Calculated %: Sb 30.57

Preparation of Crystalline Benzyllithium. A solution of tribenzylantimony was prepared by rapidly opening an ampoule of tribenzylantimony, connecting it in a countercurrent of nitrogen by a piece of flexible stout-walled rubber tubing to the apparatus, and transferring the substance. Solvent was then added, and the mixture was warmed slightly (and if cloudy was filtered in an atmosphere of nitrogen through folded filter paper that had been dried over phosphoric oxide) [7]. All operations of uniting apparatus were carried out rapidly and in such a manner that the solutions were continuously protected by the passing stream of pure dry nitrogen. The cylinder nitrogen (oxygen content not greater than 0.3%) was purified by passing through three columns of the same length containing calcium chloride, caustic potash, and phosphoric oxide on glass wool respectively.

A clear solution of tribenzylantimony (9.5 g; 1 mole) in a mixture of dry thiophene-free benzene (50 ml) and pentane (50 ml) was introduced into the special apparatus [7], which had been dried out and filled with nitrogen; the mixture was cooled to 0°. A clear, benzene solution (44.3 ml) of ethyllithium (2.59 g; 3 moles was then added from a buret through the upper exit of the apparatus, and the apparatus was closed, the reaction mixture being left overnight at 0°. The yellow color of benzyllithium appeared shortly after the solutions were mixed; a cloudiness then appeared, and a fine, lemon-yellow precipitate of benzyllithium began to come down; it readily formed large flakes, which gradually settled on the walls of the apparatus. When the reaction was carried out at room temperature, it was practically complete in one to two hours. When ethyllithium was added to the tribenzylantimony solution warmed to 30-35°, or when the reaction mixture was warmed to this temperature, the reaction was complete in 20-30 minutes. In order to filter off the precipitate of benzyllithium, a filtration apparatus having a porous glass filter [7], previously dried and filled with nitrogen, was connected to the side exit of the apparatus (the solution being protected by the passing stream of nitrogen). Nitrogen was passed through the apparatus for five minutes, and during this time the precipitate of benzyllithium was cleaned off the walls by means of a rod applied through the upper opening of the apparatus, the lumps, if any had formed, being broken up. The apparatus was closed and inverted; the precipitate was filtered. The receiver for the filtrate was connected to a drying system. The remains of the precipitate were washed out of the apparatus with a small amount of pentane, and the first apparatus was disconnected, leaving the filtration apparatus connected through a side tube to the nitrogen stream, which maintains a small pressure of nitrogen in the apparatus. Through the upper opening (opened for only a short time;) the residue was washed on the filter with three successive 20-ml portions of dry pentane, and was then stirred with a rod and, with the apparatus inclined on its side, dried in the stream of nitrogen (passing from the side tube through the filter), with occasional shaking. The receiver containing the filtrate was disconnected.

In order to obtain a dry, readily flowing preparation of benzyllithium, it was dried for about 1-1.5 hours, and the so-obtained lemon-yellow powder of benzyllithium was generally transferred through the side tube of the apparatus to a large ampoule (filled with nitrogen) for weighing and dissolution; at the same time, two or three samples for analysis were taken.

Ampoules containing samples for analysis must not be allowed to lie: analysis must be performed without delay. The same method of analysis was used as in the case of crystalline aromatic lithium compounds [7].

The preparation obtained at 0° gave, on analysis, 7.18-7.22% of lithium, and that obtained at room temperature gave 7.4-7.5% (calculated for C_7H_7Li, 7.08%). Analysis of solutions of benzyllithium was carried out by the usual method (double titration) [11].

The benzyllithium obtained (3.8-4.2 g, 50-56%) was used immediately for further reactions or was dissolved in ether. If a turbid solution was obtained, it was filtered under nitrogen and then sealed in ampoules. Benzyllithium may be preserved in the dissolved state for several days, but, in the dry state (under nitrogen, of course), it changes color and conglomerates even in one day.

SUMMARY

1. Crystalline benzyllithium has been prepared by the reaction of tribenzylantimony with ethyllithium in pentane-benzene solution. Its properties have been investigated.

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RAMAN SPECTRA OF SOME SILA-HYDROCARBONS

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Developments in the field of organosilicon compounds have presented investigators with a number of problems in the study of their chemical and physical properties, particularly the problem of the structures of these compounds. Organosilicon compounds generally differ in their properties from their hydrocarbon analogs, and the question arises of the extent to which they differ in molecular structure from the corresponding hydrocarbons.

In the solution of structural problems relating to hydrocarbons, great assistance has been given by studies of their vibrational spectra by methods of infrared and Raman spectroscopy. It is natural, therefore, to apply these methods also in the investigation of the structure of organosilicon compounds. Also, the vibrational spectrum being an exactly defined characteristic of a chemical compound (by frequencies, intensity, and state of polarization of the spectral lines), is of great assistance when carrying out molecular-spectrum analysis. Such analysis has already gained a secure place in organic chemistry, for it permits the solution of many analytical problems which cannot be solved by the available methods of chemical analysis. In the literature there are comparatively few papers devoted to the study of the Raman and infrared spectra of organosilicon compounds.

We have undertaken a study of the Raman spectra of organosilicon compounds. In this paper we give the results of a study of the Raman spectra of silanes having ethyl and methyl substituents, the following compounds being investigated:

1. Trimethylsilane $(CH_3)_3SiH$. Prepared from trichlorosilane and methylmagnesium bromide: b.p. 10.0-10.5° (b.p. 9-11° [1]).

2. Tetramethylsilane $(CH_3)_4Si$. Prepared from silicon tetrachloride and methylmagnesium bromide: b.p. 26°, d_4^{20} 0.6411; n_D^{20} 1.3578; found MR 30.11; calculated MR 30.28 [2]. Literature data b. p. 26-26.5° [3, 4, 5]; d_4^{20} 0.646 [5]; 0.6480 [4]. n_D^{20} 1.3591 [4].

3. Ethyltrimethylsilane $(CH_3)_3Si(C_2H_5)$. Prepared from trichloroethylsilane and methylmagnesium bromide: b.p. 62-62.5°, d_4^{20} 0.6851; n_D^{20} 1.3818; found MR 34.64; calculated MR 33.91 [2]. Data in the literature: b.p. 62°/760 mm; d_4^{20} 0.6849; n_D^{20} 1.3820 [6].

4. Diethyldimethylsilane $(CH_3)_2Si(C_2H_5)_2$. Prepared from dichlorodiethylsilane and methylmagnesium bromide; b.p. 95.5°; d_4^{20} 0.7168; n_D^{20} 1.4010; found MR 39.32; calculated MR 39.54 [2]. Data in the literature: b.p. 95.7-96.2°/760 mm; d_4^{20} 0.7168 [7].

5. Triethylmethylsilane $(CH_3)Si(C_2H_5)_3$. Prepared from trichloromethylsilane and ethylmagnesium bromide: b.p. 127°; d_4^{20} 0.7470; n_D^{20} 1.4160; found MR 43.67; calculated MR 44.17 [2]. Data in the literature: b.p. 127° at 760 mm; d_4^{20} 0.7473; n_D^{20} 1.4160 [6].

The Raman spectra of trimethylsilane, ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane were investigated for the first time. The spectrum of tetramethylsilane has already been described in the literature [8].

The Raman spectra of the substances investigated were photographed in a glass three-prism spectrograph (with a camera of f = 270 mm). The substance, which was contained in a cylindrical glass cell having a blackened "horn" at its end, was illuminated by the light of a PRK-2 quartz mercury lamp in an illuminating assembly (single-bulb illuminator with eliptical mirrors). The excitation was effected by radiation of λ = 4358 A. The violet part of the mercury spectrum was absorbed by a filter (saturated solution of sodium nitrite in water: a 2-cm layer). The spectra were photographed on highly sensitive plates, the time of exposure being 2-3 hours. The Raman frequencies of the substances that we investigated are given in Table 1, in which there are given also the data from the literature on tetramethylsilane [8] and tetraethylsilane [9].

TABLE 1

Raman Frequencies of the Investigated Ethyl- and Methyl-substituted Silanes (cm^{-1})

$HSi(CH_3)_3$	$Si(CH_3)_4$		$(CH_3)_3Si(C_2H_5)$	$(CH_3)_2Si(C_2H_5)_2$	$(CH_3)Si(C_2H_5)_3$	$Si(C_2H_5)_4$ Anderson [9]
		Rank and Bordner [8]				
				141(2)		
			155(5)	165(2)		160
	199(10)b	202			185(4)bd	
219(10)			212(10)b	215(5)		
251(1)	243(10)b	239	237(8)sh	237(1)d	237(4)bd	249
					279(2)d	
				299(4)	301(5)	303
			330(8)sh	330(2)	330(2)	
				358(2)		
					372(2)	
			433(0)d			393
600(5)						
623(20)	590(20)sh•	598	580(20)sh•	568(20)sh•	559(20)•	553•
				577(1)		
			664(8)sh	653(4)d	646(5)d	625
	690(10)b	696	690(10)	680(3)	678(2)d	
718(8)				704(3)		
			750(1)d		743(5)d	736
			770(1)d	776(3)d	791(2)d	
839(1)			833(3)d	825(1)d		
	859(7)b	863	860(1)d		869(0)	865
908(1)				907(0)	909(0)	
				947(0)	950(0)	
			969(3)	972(6)	969(7)	978
			1013(5)	1009(6)sh	1009(7)b	1021
						1200
			1230(1)d	1230(4)	1228(5)d	
	1249(2)d		1249(3)d	1247(1)	1246(1)	
1258	1260(2)d	1264				
1414	1418(7)d	1427	1411(8)	1406(8)	1410(8)d	1423
			1461(5)	1458(8)	1461(10)d	1467
2118(10)						
				2735(2)	2735(2)	2734
						2813
			2881(20)b	2880(20)b	2881(20)b	2885
2902(10)	2898(20)b	2905	2897(20)b	2904(20)b	2899(20)b	2912
				2944(1)		
2967(10)	2957(20)b	2963	2957(20)b	2959(20)b	2958(20)b	2950

Note: In parentheses are given the relative intensities, as estimated visually, of the lines, the intensity of the 1246 cm^{-1} line in the spectrum of triethylmethylsilane being taken as unity.

The symbols used are: b, broad; sh, sharp; d, diffuse.

In the present stage of the investigation it is not possible to give a full interpretation of the spectra of these substances. A fairly full interpretation has been given only of the spectrum of tetramethylsilane, following the analogy with the spectrum of tetramethylmethane [10]. In the spectra of the organosilicon compounds that we have investigated, as in the spectra of hydrocarbons, there are frequencies attributable to the valency and

TABLE 2

Frequencies of C–H Valency Vibrations

Isobutane [1]	Trimethylsilane	Tetramethylmethane [8]	Tetramethylsilane	2,2-Dimethylbutane [12]	Ethyltrimethylsilane	3,3-Dimethylpentane	Diethyldimethylsilane	3-Ethyl-3-methylpentane [12]	Triethylmethylsilane
								2663	
2628		2712		2713		2674		2734	
2718		2745		2739		2712		2857	2735
2778		2794		2855		2736	2735	2883	2881
2868		2864		2870	2831	2855		2897	
2906	2902	2892	2898	2893	2897	2864	2880	2915	2899
2936		2911		2904		2890	2904	2932	
2959		2937		2942		2907		2943	
	2967	2955	2957	2963	2957	2942	2944	2966	2957
						2967	2959		

deformation vibrations of the methyl group. Frequencies in the region 1230-1260 cm^{-1} are those due to the vibration of the methyl group, and the frequency of about 1415 cm^{-1} relates to the deformation vibration of H–C–H of the CH_3 group; the frequency of about 1460 cm^{-1} is that of the deformation vibration of H–C–H of the CH_2 group.

In the region of high displacements (2700-3000 cm^{-1}) lie the frequencies of the valency vibrations of C–H (of CH_2 and CH_3 groups). It should be noted that in the spectra of organosilicon compounds the number of these frequencies is considerably smaller than in the spectra of their hydrocarbon analogs (see Table 2) and corresponds to the number of frequencies to be expected from the results of calculation [13]. According to these calculated results, the group CH_3 should have two valency frequencies: symmetrical 2902 cm^{-1} and degenerate 2983 cm^{-1}. The group CH_2 should also have two frequencies: symmetrical 2884 cm^{-1} and antisymmetrical 2922 cm^{-1}.

Actually, in the spectra of trimethylsilane and tetramethylsilane we observed in each case two frequencies: about 2900 and 2960 cm^{-1}. The frequency of about 2900 cm^{-1} is evidently that of the symmetrical vibration of the group CH_3, and the frequency of about 2960 cm^{-1} must evidently be assigned to the degenerate vibration of the group CH_3.

Two frequencies, due to the methyl group, were observed also in the spectra of ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane: about 2900 cm^{-1} and about 2960 cm^{-1}. A frequency of 2880 cm^{-1}, evidently the frequency of the symmetrical vibration of the CH_2 group, was observed also. The antisymmetrical frequency of the CH_2 group did not appear, and only in the case of diethyldimethylsilane did we find a faint line at 2944 cm^{-1}, which could be assigned, evidently, to the antisymmetrical vibration of the CH_2 group. A frequency of 2735 cm^{-1} appeared in the spectra of compounds containing several ethyl groups.

The frequency 2118 cm^{-1} in the spectrum of trimethylsilane is the frequency of the valency vibration of Si–H. In comparison with the frequency of the analogous vibration in silane SiH_4 (2180 cm^{-1}), this frequency is displaced by 60 cm^{-1}.

According to Kohlrausch's interpretation [10], the frequency of 590 cm^{-1} in the spectrum of tetramethylsilane is the frequency of the fully symmetrical vibration of Si–C. In the spectra of the substances that we investigated, this frequency (region 550-600 cm^{-1}), in passing from tetramethylsilane to tetraethylsilane, undergoes a characteristic displacement: as methyl groups are successively replaced by ethyl groups, this frequency alters in value by jumps of about 10 cm^{-1} (this frequency is marked by an asterisk in Table 1). In the spectrum of trimethylsilane this frequency has the value 623 cm^{-1}. In conclusion, we draw attention to the fact that in the spectrum of tetramethylsilane we observed two frequencies, 1249 and 1260 cm^{-1} instead of one, 1264 cm^{-1}, observed by Rank and Bordner [8].

SUMMARY

1. The Raman spectra of the following compounds have been investigated: trimethylsilane, tetramethylsilane, ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane.

2. The frequencies of valency and deformation vibrations of the groups CH$_2$ and CH$_3$ lie in the same region of the spectrum as in the case of their hydrocarbon analogs.

3. The number of frequencies associated with the valency vibrations of the C–H group of CH$_2$ and CH$_3$ in the spectra of the sila-hydrocarbons investigated is less than in the spectra of their hydrocarbon analogs and corresponds to the number of frequencies to be expected from calculation data.

4. The frequency of the fully symmetrical vibration of Si–C diminishes as methyl groups are replaced by ethyl groups in the compounds investigated.

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USE OF THE SALT $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ IN THE DOUBLE-DIAZONIUM-SALT METHOD

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In the double-diazonium-salt method for the synthesis of organoantimony compounds, which was developed by one of us in conjunction with Kocheshkov [1], the initial diazonium compounds were May's salts $ArN_2Cl \cdot SbCl_3$ (Ar being phenyl, p-tolyl, o-, m-, or p-chlorophenyl, p-bromophenyl, p-iodophenyl, o- or p-anisyl, or p-phenetyl), which, when decomposed with zinc dust in boiling ethyl acetate, yield, as a rule, several products. The predominating reaction is the formation of a monoaryl derivative of tervalent antimony; formation of diarylstibinous chloride and triarylstibine dichloride proceeds to an appreciable extent; and triarylstibine is formed in insignificant amount.

Reutov and Ptitsyna [2] have since shown that formation of triarylstibine dichloride in the double-diazonium salt method is a secondary reaction, which can be avoided by working up the reaction products in absence of air or at room temperature. Under these conditions only mono- and di-aryl derivatives of tervalent antimony are formed. The same authors have found also that, if after decomposition of May's salt under the usual conditions of the diazo method a further amount of May's salt is added to the reaction mixture, then the sole reaction product is a derivative of quinquevalent antimony—diphenylstibinic acid (after hydrolysis)**.

It was natural to expect that the decomposition of a double diazonium salt differing in composition from May's salt, namely one in which there are two molecules of arenediazonium salt per molecule of antimony trichloride, i.e. $(ArN_2Cl)_2 \cdot SbCl_3$, would favor the formation of polyaryl antimony derivatives as main products of the reaction. When attempts were made to obtain a salt of this composition by reaction of two moles of benzenediazonium chloride, prepared by diazotizing aniline in a solution of hydrochloric acid, with one molecule of antimony trichloride, only May's salt was obtained. A double diazonium salt of the composition $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ was obtained in 80% yield by diazotizing two moles of aniline hydrochloride in a methanolic solution of amyl nitrite and pouring the diazo solution obtained into a methanolic solution of antimony trichloride (one mole).

When this salt was decomposed under the conditions used for the preparation of organoantimony compounds by the diazo method [1] (zinc in boiling ethyl acetate), the predominant reaction product was diphenylstibinous chloride (40% yield), which was accompanied by a very small amount of phenylstibinous dichloride. Decomposition of the salt $(C_6H_5N_2Cl_2) \cdot SbCl_3$ with zinc and ethanol, like that of May's salt with zinc in this solvent, gives a mixture of products, the principal one being a derivative of quinquevalent antimony—triphenylstibine dichloride. Decomposition of this salt in other solvents (acetone, benzene, chloroform, amyl acetate, diisopentyl ether, methyl formate, methanol) and in ethyl acetate with metals other than zinc (powders: antimony, copper, iron, magnesium, aluminum; aluminum and zinc amalgams and zinc-copper alloy) reduces the yield of diphenylstibinous chloride at the expense of a monophenyl derivative of tervalent antimony and triphenylstibine dichloride (Tables 1 and 2).

It was found also that, if in the synthesis of organoantimony compounds the stage involving isolation of the double diazonium salt is cut out by carrying out the diazotization of aniline hydrochloride in presence of antimony trichloride and a small amount of hydrochloric acid by means of sodium nitrite in ethyl acetate and decomposing the reaction mixture obtained with zinc, then the sole reaction product is triphenylstibine, obtained in 50-54% yield; this constitutes a new method for the preparation of this compound via a diazo compound. Triphenylstibine is the sole reaction product also when the decomposition is brought about under these conditions in presence of sodium sulfate as dehydrating agent. When decomposition is effected in presence of calcium chloride, triphenylstibine formation is supplanted by formation of triphenylstibine dichloride, which is obtained in 46% yield.

EXPERIMENTAL

Preparation of the Double Diazonium Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$. Aniline hydrochloride (52 g, 0.4 mole) was dissolved in methanol (200 ml) and, under cooling to −5° and mechanical stirring, was diazotized with amyl nitrite (52 g—a small excess) at such a rate that the temperature did not rise above −2°. Ten to fifteen

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*Deceased.

** The present work was carried out without taking the results of Reutov and Ptitsyna into account.

TABLE 1

Decomposition of the Double Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ in Various Solvents*

Solvent (50 ml)	Initial temp. (°C)	Yield on phenyl (%)			Utilization of phenyl (%)	Notes
		R_2SbCl	RSbO	R_2SbAc		
Ethanol	40-50	15.2	6.4	3.7	25.3	Very vigorous decomposition
Acetone	50	6	1.6	13.2	20.5	Ditto
Benzene	70	Traces				Very feeble decomp., not complete even after several hours
Chloroform	60	6	0.8	5.1	11.9	Very feeble decomp., heat reqd., salt not wholly decd. after several hrs.
Amyl acetate	130	2.4	2.4	17.2	22.0	Very vigorous decomposition
Diisopentyl ether	100	–	3.2	Traces	3.2	Vigorous decomposition
Methanol	60	–	1.2	13	14.2	Vigorous decomposition
Methyl formate	10.5	–	10	12.5	22.5	Ditto
Water	75	Traces	–	–	–	About 20% phenol obtained.
Liquid ammonia	Cooled with solid CO_2 and ether	–	–	–	–	Very vigorous decomposition

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* For the decomposition, 15 g of double salt and 7 g Zn were taken.

minutes after addition of amyl nitrite was complete, a solution of antimony trichloride (45.6 g, 0.2 mole) in methanol (60 ml) was added. The precipitated double salt was filtered off under suction, washed twice with a small amount of methanol, twice with ether, and then dried in the air. The yield was 82-87 g).

The double diazonium salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ is a yellow powder, only slightly soluble in alcohol and acetone, decomposed by water, slightly soluble in ethyl acetate, insoluble in ether and chloroform. It decomposes at about 100°. It is stable to percussion and to temperatures of up to 40°.

Found %: N 10.18; 10.02; Sb 24.24; 23.33
$(C_6H_5N_2Cl_2)_2 \cdot SbCl_3$. Calculated %: N 10.99; Sb 23.91
$C_6H_5N_2Cl \cdot SbCl_3$. Calculated %: N 7.59; Sb 33.04

Preparation of Diphenylstibinous Chloride. The decomposition of the double diazonium salt was carried out in a special vessel consisting of a 1-1.5-liter three-necked round-bottomed flask having at the bottom a cylindrical constriction (1/12-1/14 of the total volume of the flask) in which the whole of the reaction mixture was placed. The upper part of the flask was intended for the froth formed during decomposition. The flask was fitted with a Witt stirrer, the widened part of which corresponded to the lower part of the flask. The use of a vessel of this form permitted the reaction mixture to be cooled as quickly as possible at the end of the first, violent stage of the decomposition by immersing the constricted part in ice water, and it also ensured thorough stirring of the reaction mixture important to the yield. The salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ (15 g) and ethyl acetate (50 ml) were introduced into the constricted part of the flask and the mixture was stirred while zinc dust (7 g, i.e. double the theoretical amount) was poured in. Vigorous decomposition with copious frothing occurred, and the temperature rose to 75-78°. When the froth began to subside, the vessel was cooled externally with iced water, correctly timed cooling being very important: it must not be too early, or the final stage of decomposition will be affected. The whole decomposition was complete in a few seconds. When the mixture had cooled, it was filtered from the excess of zinc, and the greater part of the ethyl acetate was driven from the filtrate at somewhat reduced pressure. The solution was diluted with five times its bulk of ethanol or methanol and was poured into aqueous ammonia and ice (50 ml 25% NH_4OH, 100 ml water, 100 g ice). A sticky precipitate came down and was given several hours to settle. The greater part of the liquid was poured off, the precipitate was filtered off, and diphenylstibinous chloride was extracted from it by washing with chloroform or dichloroethane. The chloroform was driven off on a water bath, the remaining oil (diphenylstibinous chloride) was treated with a small amount of concentrated hydrochloric acid in presence of alcohol, and the precipitate was filtered off and dried; yield 42-46%. Melting point after two crystallizations from chloroform, 67-68°.

TABLE 2

Decomposition of the Double Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ by Various Metals*

Initial temp. (°C)	Metal	Character of decomp.	Yield (%)			Utilization of C_6H_5 (%)	Notes
			R_3SbCl_2	RSbO	R_2SbAc		
75	Fe	Vigorous	–	11	Traces	11	At lower temp. decomp. is feeble
75	Sb	Moderate	12	28	3	43	It is necessary to warm to initiate decomp.
70	Cu	Moderate	Traces	12	Traces	12	Part of salt did not decompose, in spite of warming
65	Mg	Vigorous, after warming	–	2.8	7.0	9.8	
70	Al	Feeble: warming necessary during decomp.	–	8.8	–	8.8	
70	Al/Hg**	Decomp. feeble for 40 min., then more vigorous	–	8.8	–	8.8	Was warmed slightly during decomp.
70	Zn/Cu**	Very vigorous	7.2	4	14.2	25.4	
70	Zn/Hg**	Vigorous	–	5.6	10.0	15.6	

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* For the decomposition, 15 g of double salt and double the theoretical amount of metal were taken; solvent: 50 ml of ethyl acetate.

** The couples Al/Hg, Zn/Hg, Zn/Cu – amalgamated Al and Zn, coppered Zn.

Preparation of Triphenylstibine. Sodium nitrite (3.7 g) was added with stirring to a cooled (+5 – +10°) mixture of aniline (4.65 g), antimony trichloride (5.75 g), ethyl acetate (45 ml), and concentrated hydrochloric acid (10 ml). When addition of nitrite was complete, the reaction mixture was set aside for 40-45 minutes to enable reaction to proceed to completion. Zinc dust (6.5 g) was then added with stirring to the reaction mixture, which, owing to the fact that it contained water, was viscous. Decomposition set in immediately and proceeded very quickly without much foaming, so that the whole operation could be carried out in an ordinary beaker. When decomposition was complete, the reaction mixture was rapidly cooled externally with ice and then filtered from the zinc. The filtrate was placed in a Wurtz flask, and ethyl acetate was driven off under somewhat reduced pressure until the volume of the reaction mixture was reduced to 20 ml. It was then treated twice with 5N HCl (20 and 10 ml), and the acid aqueous layer was separated. The ethyl acetate solution was poured into a mixture of aqueous ammonia and ice (42 ml 25% NH_4OH, 25 ml water, 130 g ice). The precipitated yellowish oil, after being allowed to stand overnight, was separated from the completely clear aqueous layer and extracted with chloroform. Under these conditions dissolution was almost complete, which in itself showed that practically no phenylstibinous dichloride was formed. When solvent had been removed, the oil that remained was converted by treatment with acetic acid into pale-yellow crystals (yield of triphenylstibine, 50%). After crystallization from petroleum ether, the melting point, and the mixed melting point with authentic triphenylstibine, was 52°.

Preparation of Triphenylstibine Dichloride. The procedure was the same as in the preceding experiment on the preparation of triphenylstibine. After completion of diazotization, calcium chloride (20 g) was added, and the reaction mixture was stirred for 1-2 hours and then decomposed. The usual treatment yielded triphenylstibine dichloride (3.25 g, 46.2%), m.p. 139-142°. At the same time a small amount of a diphenylated tervalent antimony compound was formed: it was isolated as diphenylstibinous acetate (acetyldiphenylstibine) (0.7 g).

SUMMARY

1. A double diazonium salt of the composition $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ has been prepared.

2. When this salt is decomposed with zinc and ethyl acetate, diphenylstibinous chloride is formed in 42-46% yield.

3. When $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ is decomposed with zinc in acetone, methanol, methyl formate, benzene, chloroform, amyl acetate, or diisopentyl ether, or is decomposed in ethyl acetate with the following metals in powder form: copper, iron, antimony, aluminum, or magnesium, with the amalgam of aluminum or zinc, or with an alloy of zinc and copper, phenylstibinous dichloride and triphenylstibine dichloride are formed, as well as diphenylated antimony compounds. Triphenylstibine dichloride is the main reaction product in the decomposition of both the salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ and also May's salt with zinc in ethanol.

4. A method has been found for the preparation by the diazo method of triphenylstibine, which is formed in 50% yield by the decomposition with zinc of the reaction mixture containing the double diazonium salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ obtained by diazotizing aniline with sodium nitrite in ethyl acetate in presence of antimony trichloride and hydrochloric acid.

5. When this decomposition reaction is carried out in presence of calcium chloride, triphenylstibine dichloride is obtained in 46% yield.

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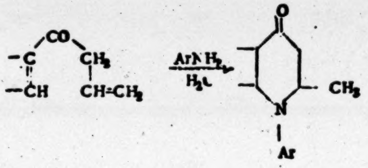
[2] O. A. Reutov and O. A. Ptitsyna, Rep. Acad. Sci. USSR, 79, 819 (1951).

ACETYLENE DERIVATIVES

COMMUNICATION 148. HETEROCYCLIC COMPOUNDS
XXV. SYNTHESIS OF SECONDARY AND TERTIARY 2,5-DIMETHYL-1-PHENYL-4-PIPERIDINOLS AND THEIR ESTERS*

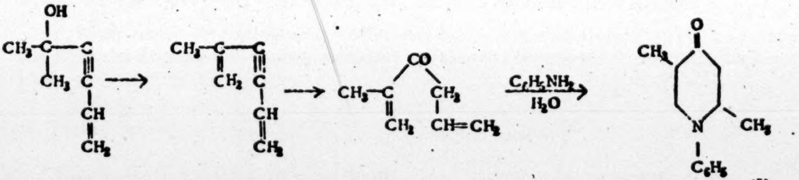
I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

In one of our previous communications we have described a simple method for the preparation of various 1-aryl-4-piperidones: cyclization of allyl vinyl ketones by reaction with primary aromatic amines in presence of water [1]:



1-Aryl-4-piperidones have thus become quite accessible and may now be used widely in syntheses of related compounds of the piperidine series. We considered that it would be of interest to examine the effect of the aromatic residue at the nitrogen on the physiological activity of esters of 4-piperidinols.

In this paper we describe the synthesis of secondary and tertiary 2,5-dimethyl-1-phenyl-4-piperidinols and of a number of their esters. The starting material for these syntheses was 2,5-dimethyl-1-phenyl-4-piperidone (I), which is readily prepared from commercially available ethynyldimethylvinylmethanol and aniline, following the following scheme:



(I)

When 2,5-dimethyl-1-phenyl-4-piperidone (I) was reduced with sodium in moist ether or sodium in absolute alcohol, or was hydrogenated in presence of a platinum or nickel catalyst, a mixture of the stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidinols (II) was formed in good yield; it was separated by crystallization from benzene into α- and β-forms, melting respectively at 75-76° and 81-82°.

When the hydrochloride of the piperidone (I) was hydrogenated in presence of a platinum catalyst under normal conditions, only one 2,5-dimethyl-1-phenyl-4-piperidinol hydrochloride (m.p. 266-267°) was obtained; it corresponded to the low-melting base (m.p. 75-76°): (see benzene rings top of next page).

In presence of powdered caustic potash, 2,5-dimethyl-1-phenyl-4-piperidone (I) dissolved in dry ether was found to condense with acetylene, forming 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III) in 50% yield. The latter was converted by exhaustive hydrogenation of the acetylenic linkage in presence of a platinum

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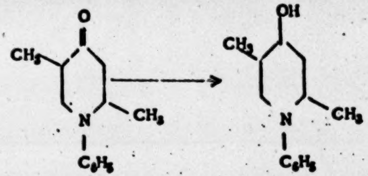
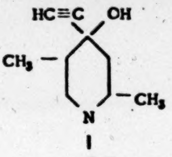
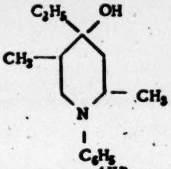


(I) (II)

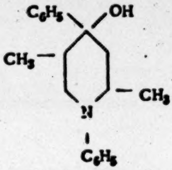
catalyst into 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (m.p. 60-61°; hydrochloride, m.p. 205-206°). By the action of ethylmagnesium bromide on the piperidone(I,) the second stereoisomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) was obtained in 45% yield as a liquid (hydrochloride, m.p. 186-187°):



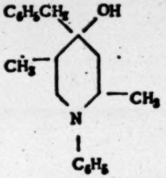
(III)



(IV)



(V)

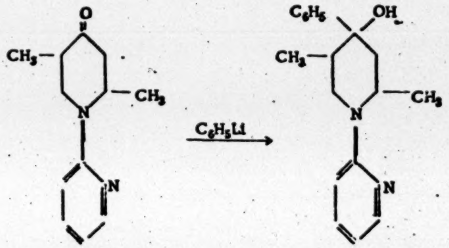


(VI)

By the action of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I), 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V) was formed in 83% yield; it was isolated in only one stereoisomeric form. 4-Benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI) was prepared, also only in one stereoisomeric form, in 74% yield by the Grignard reaction, i.e. by the action of benzylmagnesium chloride on the piperidone(I).

Thus, all the above described reactions of 2,5-dimethyl-1-phenyl-4-piperidone (I) (catalytic hydrogenation of the hydrochloride, condensation with acetylene, reaction with phenyllithium and benzylmagnesium chloride) proceed in a sterically selective fashion, and in each case lead to the formation of only one stereoisomer. This behavior of 2,5-dimethyl-1-phenyl-4-piperidone is in marked contrast with that of 1-alkyl-2,5-dimethyl-4-piperidones, which always give mixtures of two or three stereoisomers in similar reactions.

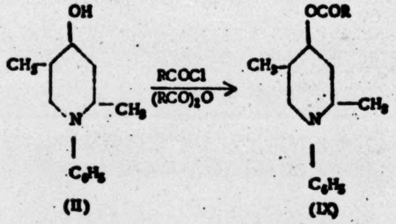
By the action of phenyllithium on 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII) [1], 2,5-dimethyl-4-phenyl-1-(2-pyridyl)4-piperidinol (VIII) is obtained in high yield; this also is isolated in only one stereoisomeric form:



(VII) (VIII)

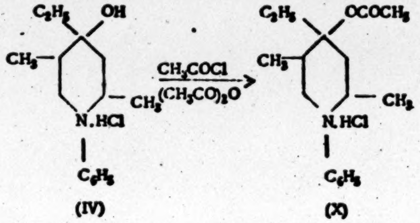
This reaction, like that of 2,5-dimethyl-1-phenyl-4-piperidone, has therefore also a sterically selective character.

By the esterification of the two stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (II) with anhydrides or acid chlorides of acetic, propionic, benzoic, and p-nitrobenzoic acids, the corresponding esters were obtained. The p-nitrobenzoate was catalytically reduced in presence of platinum to the p-aminobenzoate. The esterification of the high-melting form of 2,5-dimethyl-1-phenyl-4-piperidinol was carried out by Spassow's method [2] in benzene solution in presence of magnesium turnings.

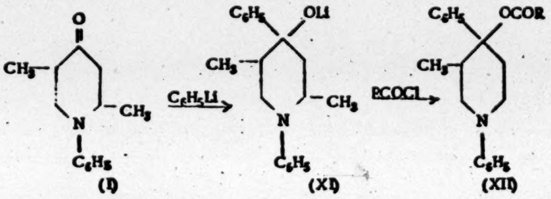

OH
CH$_3$
CH$_3$
N
C$_6$H$_5$
(II)
RCOCl
(RCO)$_2$O
OCOR
CH$_3$
CH$_3$
N
C$_6$H$_5$
(IX)

R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$, p-O$_2$NC$_6$H$_4$, p-H$_2$NC$_6$H$_4$

The hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV), prepared by the Grignard reaction, was acetylated with a mixture of acetyl chloride and acetic anhydride in presence of magnesium. The hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol acetic ester (X) separated directly after the reaction in the form of long rods (25-30 mm):


C$_2$H$_5$
OH
CH$_3$
CH$_3$
N.HCl
C$_6$H$_5$
(IV)
CH$_3$COCl
(CH$_3$CO)$_2$O
C$_2$H$_5$
OCOCH$_3$
CH$_3$
CH$_3$
N.HCl
C$_6$H$_5$
(X)

The esters (acetate, propionate, and benzoate) of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII) were obtained by the action of the acid chlorides or anhydrides of the corresponding acids on the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XI), which was obtained by the action of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I):


O
CH$_3$
CH$_3$
N
C$_6$H$_5$
(I)
C$_6$H$_5$Li
C$_6$H$_5$
OLi
CH$_3$
CH$_3$
N
C$_6$H$_5$
(XI)
RCOCl
C$_6$H$_5$
OCOR
CH$_3$
N
C$_6$H$_5$
(XII)

R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$

All the esters of secondary and tertiary 1-phenyl-4-piperidinols that we prepared were converted for pharmacological tests into the hydrochlorides by saturation of their ether solutions with dry hydrogen chloride. The hydrochlorides of these esters are colorless crystalline substances, soluble, in various degrees, in water. The esters described in this paper were without anesthetic action, with the exception of the esters (IX) (α-form, R = CH$_3$) and (X), which were approximately equivalent to novacaine in anesthetic activity, but had an irritating effect on the mucous membrane. The compounds (XII)(R = C_2H_5 and C_6H_5) were not tested, because of the insolubility of their hydrochlorides in water.

EXPERIMENTAL

Hydrogenation of 2,5-Dimethyl-1-phenyl-4-piperidone in Presence of a Platinum Catalyst

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (b.p. 116-118°/1 mm; n_D^{20} 1.5521) (39 g) in absolute alcohol (80 ml) was hydrogenated in presence of a Pt catalyst prepared according to Adams. In the course of 26 hours, 4050 ml (20°, 746 mm) of hydrogen was absorbed instead of 4817 ml, as required theoretically. The catalyst was filtered off, the alcohol was driven off, and the product was vacuum-distilled. The product consisted of 30.5 g of a mixture of stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidinols (II), b.p. 115-120° at 0.5 mm, in the form of a colorless viscous liquid, which, after standing for a short time, solidified (m.p. 50-54°). The product was of good solubility in alcohol, benzene, gasoline, acetone, chloroform, methanol, but was insoluble in water. After being dissolved in petroleum ether (b.p. 40-60°) and then cooled to −25°, the product separated as a gelatinlike mass, which was converted, on being dried, into a powder, m.p. 69-72°.

Found %: C 76.46; 76.59; H 9.53; 9.42

$C_{13}H_{19}ON$. Calculated % C 76.14; H 9.33

Dry hydrogen chloride was passed through an ether solution containing 25 g of the mixture of isomeric 2,5-dimethyl-1-phenyl-4-piperidinols (m.p. 50-54°). The hydrochloride that separated (18.2 g) melted after being recrystallized twice from 95% alcohol at 266-267°.

Found %: N 5.86; 5.79

$C_{13}H_{20}ONCl$. Calculated %: N 5.79

The hydrochloride of m.p. 266-267° (18 g) was dissolved in water, and the free base was precipitated with 25% aqueous ammonia and extracted with ether. The ether extract was dried over sodium sulfate. Fractionation of the ether solution yielded 14.1 g of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 75-76° (from petroleum ether).

Found %: N 6.99; 7.24

$C_{13}H_{19}ON$. Calculated %: N 6.82

The picrate of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol melted at 177-178.5° (from alcohol).

Found %: N 13.10; 12.90

$C_{19}H_{22}O_8N_4$. Calculated %: N 12.90

Hydrogenation of the Hydrochloride of 2,5-Dimethyl-1-phenyl-4-piperidone (I) in Presence of a Pt Catalyst

2,5-Dimethyl-1-phenyl-4-piperidone hydrochloride (m.p. 157-158°) (4.35 g) dissolved in alcohol (50 ml) was hydrogenated in presence of an Adams Pt catalyst. In the course of 18 hours, 370 ml (757 mm, 19°) of hydrogen was absorbed, against 390 ml calculated. The catalyst was filtered off. When the solvent had been distilled off, colorless crystals came down; they were recrystallized from alcohol. The product consisted of 3.8 g of the above-described hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II); it melted at 266-267°, alone and in admixture with the previous sample.

Reduction of 2,5-Dimethyl-1-phenyl-4-piperidone (I) with Sodium in Moist Ether

A mixture of 2,5-dimethyl-1-phenyl-4-piperidone (m.p. 117-118° at 1 mm; n_D^{20} 1.5522) (58 g), water (120 ml), and ether (500 ml) was introduced into a three-necked flask fitted with mercury-sealed stirrer and condenser. Sodium (67 g) in the form of small pieces was introduced into the flask under continuous stirring in such a way as to maintain the ether at a steady boil. When the whole of the sodium had been dissolved, water (100 ml) was added to the reaction mixture under vigorous stirring. The ether layer was separated and dried with sodium sulfate. Fractionation of the ether solution yielded 50.1 g of a mixture of the stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 122-130° at 0.8 mm, in the form of a very viscous, colorless liquid, which crystallized after standing for a short time. A mixture of the product

(50 g, m.p. 50-75°) with gasoline (120 ml, b.p. 60-90°) was heated to the boil. When the solution was cooled, colorless crystals separated. A yield of 24 g of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 81-82° (from gasoline) was obtained.

Found %: C 75.90; 76.14; H 9.58; 9.48
$C_{13}H_{19}ON$. Calculated %: C 76.14; H 9.33

A mixed test with the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (b.p. 75-76°) melted at 47-64°.

The hydrochloride of the high-melting 2,5-dimethyl-1-phenyl-4-piperidinol was prepared by passage of dry hydrogen chloride through an ether solution of the base (m.p. 81-82°). The sticky precipitate obtained was gradually converted into a white powder, m.p. 170-171° (from absolute alcohol), by boiling it with dry acetone.

Found %: N 6.04; 6.17
$C_{13}H_{20}ONCl$. Calculated %: N 5.79

The high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol did not give a picrate.

The gasoline mother liquor, after separation of the high melting isomer of the piperidinol(II) was diluted with absolute ether and saturated with dry hydrogen chloride. The hydrochloride that separated was recrystallized from 95% alcohol. The product was the hydrochloride (24.8 g) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) having m.p. 265-267°, and it gave no depression with the above-described sample.

Hydrogenation of 2,5-Dimethyl-1-phenyl-4-piperidone (I) Hydrochloride in Presence of Raney Nickel

2,5-Dimethyl-1-phenyl-4-piperidone hydrochloride (23 g, m.p. 157-153°) in alcohol (100 ml) was hydrogenated in a rotating 156 ml autoclave in presence of Raney nickel, the initial pressure of hydrogen being 80 atm. Hydrogenation began at 100-120° and was complete in 3 hours 30 minutes. The catalyst was filtered off, the alcohol was driven off, and the residue was treated with a 50% solution of caustic alkali. The free base that separated was extracted with ether, dried with sodium sulfate, and vacuum-distilled. The product was a noncrystallizing mixture of the stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (16 g) in the form of a very viscous liquid, m.p. 105-110° at 0.2 mm.

By the action of dry hydrogen chloride on an ether solution of the base and recrystallization of the salt obtained from alcohol, the hydrochloride (10 g) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) of m.p. 266-267° was obtained. In a mixed test with the above-described preparation, there was no depression in melting point.

Reduction of 2,5-Dimethyl-1-phenyl-4-piperidone with Sodium in Absolute Alcohol

Sodium (24 g) was added in small pieces to a solution of 2,5-dimethyl-1-phenyl-4-piperidone (m.p. 116-118° at 1 mm) (15 g) in absolute alcohol (300 ml). When the sodium had dissolved to give the ethoxide, water (100 ml) was added, and concentrated hydrochloric acid (115 ml) was added slowly with stirring until the reaction was acid. The solution of salts obtained after driving off the alcohol was evaporated in a dish on a water bath and was then filtered while hot from sodium chloride. The filtrate (about 150 ml) was saturated with alkali and extracted three times with ether. The ether solution was dried with sodium sulfate, and the residue remaining after removal of the ether was vacuum-distilled, yielding a mixture (11 g) of isomeric 2,5-dimethyl-1-phenyl-4-piperidinols, m.p. 120-126° at 1 mm, in the form of a very viscous liquid, which partially crystallized out after long standing.

The mixture of isomers was boiled with gasoline and, from the cooled solution, 6.5 g of the high-melting isomer of II, m.p. 81-82°, separated; then, by saturation of the mother liquor with dry hydrogen chloride and crystallization of the salt formed from alcohol, the hydrochloride (2.4 g, m.p. 266-267°) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) was isolated.

4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III)

Dry powdered caustic potash (13 g) and dry ether (240 ml) were introduced into a three-necked flask fitted with mercury-sealed stirrer, reflux condenser, tube for the passage of acetylene, and a thermometer. The ether, which was cooled with a mixture of ice and salt (−12°), was saturated with acetylene in the course of an hour, and then, under stirring and simultaneous passage of acetylene, 2,5-dimethyl-1-phenyl-4-piperidone (m.p. 116-118° at 1 mm; n_D^{20} 1.5520) (32 g) dissolved in ether (50 ml) was added over a period of one hour. When the ketone had been added, stirring was continued, with cooling with ice water and simultaneous passage of acetylene, for a further three hours. Passage of acetylene was then discontinued, and stirring of the reaction mixture was continued for a further hour at room temperature.

The product was treated with water (80 ml), the ether layer was separated, and the aqueous layer was saturated with solid caustic potash and carefully extracted with ether. The ether extracts were dried over sodium sulfate, and the residue remaining after removal of ether was vacuum-distilled, yielding a substance of b.p. 120-125° at 0.8 mm in the form of a very viscous liquid (25 g). This was converted by fractional precipitation into the hydrochloride. After recrystallization from absolute alcohol, 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol hydrochloride (21 g), m.p. 216.5-217.5°, was obtained.

Found %: N 5.53; 5.27
$C_{15}H_{23}ONCl$. Calculated %: N 5.26

By the action of aqueous ammonia on the pure hydrochloride (m.p. 216.5-217.5°), the free base 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III), m.p. 56-57° (from petroleum ether), was prepared.

Found %: N 6.17; 6.44
$C_{15}H_{19}ON$. Calculated %: N 6.10

4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol gave a characteristic precipitate with ammoniacal silver nitrate solution.

4-Ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV)

a) 4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III) (m.p. 56-57°) (1 g) was dissolved in absolute alcohol (10 ml) and exhaustively hydrogenated in presence of an Adams platinum catalyst. In the course of one hour 215 ml of hydrogen (747 mm, 22°) was absorbed instead of 221 ml, as required by theory.

The catalyst was filtered off. The alcohol was distilled off, and the residue was dissolved by heat in gasoline; the solution, on being cooled, yielded colorless crystals, which were recrystallized from gasoline, yielding 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (0.8 g), m.p. 60-61°, as colorless crystals in the form of long rods.

Found %: N 6.15; 6.31
$C_{15}H_{23}ON$. Calculated %: N 5.99

The hydrochloride of this isomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol melted at 205-206° (from alcohol).

Found %: N 5.27; 5.22
$C_{15}H_{24}ONCl$. Calculated %: N 5.19

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (10 g) in absolute ether (15 ml) was added dropwise to a solution, cooled with ice and salt, of ethylmagnesium bromide, which was prepared from magnesium turnings (1.2 g), ethyl bromide (6 g), and absolute ether (26 ml). When addition of the piperidone was complete, stirring was continued for one hour at room temperature and for a further two hours at the boiling point of ether. The reaction mixture was treated with 18% hydrochloric acid (30 ml). The ether layer was separated, and the aqueous layer was saturated with caustic potash and extracted with ether. The ether extract was dried over magnesium sulfate, and the residue remaining after removal of ether was vacuum-distilled, yielding 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (8 g) as a very viscous colorless liquid, b.p. 110-112°/0.3 mm. The ether solution of the base was saturated with hydrogen chloride, and the salt that separated was recrystallized from a mixture of alcohol and ethyl methyl ketone, yielding 6 g of the hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 186-187°, in the form of fine glistening crystals, which were soluble in water.

Found %: N 5.27; 5.16
$C_{15}H_{24}ONCl$. Calculated %: N 5.19

4-Benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI)

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (I) (20 g) in absolute ether (30 ml) was added dropwise to a solution, cooled with ice water, of benzylmagnesium chloride, which was prepared from magnesium turnings

(2.4 g), benzyl chloride (12.7 g), and absolute ether (50 ml). When addition of the piperidone was complete, stirring was continued for 40 minutes at room temperature and then for one hour at the boiling point of ether. The reaction product was decomposed with 18% hydrochloric acid (60 ml), and the precipitated oily material was separated and treated with acetone. The crystals of hydrochloride that separated were recrystallized from alcohol, yielding 24 g of the hydrochloride of 4-benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI) as colorless crystals, insoluble in water, m.p. 222-224°.

Found %: N 4.20; 4.45
$C_{20}H_{26}ONCl$. Calculated %: N 4.22

2,5-Dimethyl-1,4-diphenyl-4-piperidinol (V)

The whole experiment was carried out in a stream of nitrogen. Absolute ether (40 ml) and fine lithium turnings (1.6 g) were introduced into a three-necked flask fitted with stirrer, reflux condenser, dropping funnel, thermometer, and a tube for the passage of nitrogen. Bromobenzene (1.5 g) was added to the mixture, and when the reaction had set in a further 16 g of bromobenzene, dissolved in absolute ether (50 ml), was added gradually. Absolute ether (150 ml) was then added to the mixture, and the reaction mixture was heated for two hours at the boiling point of ether.

When reaction was complete, the flask containing the phenyllithium was cooled to −12°, and a solution of 2,5-dimethyl-1-phenyl-4-piperidone (15 g) in ether (20 ml) was added dropwise with stirring over a period of 50 minutes. The contents of the flask were stirred at room temperature for two hours and then at the boiling point of ether for two hours. The reaction product was acidified with 15% hydrochloric acid at 0°, when a dark-colored precipitate formed at the bottom of the flask. After separation of the ether and water layers, this precipitate was treated with acetone. The crystals of hydrochloride that were isolated were recrystallized from propyl alcohol, yielding 19.5 g of the hydrochloride of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V), m.p. 237-238.5°.

Treatment of this hydrochloride (m.p. 237-238.5°) with 25% aqueous ammonia yielded 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V), m.p. 108-108.5° (from a mixture of gasoline and ethyl methyl ketone).

Found %:	H 8.43; 8.45;	C 80.60; 80.40;	N 5.32; 5.28
$C_{19}H_{23}ON$. Calculated %:	H 8.53;	C 81.04;	N 4.98

The hydrobromide, obtained by saturation of an ether solution of the base with dry hydrogen bromide, melted at 238-240° (from alcohol).

Found %: N 3.97; 3.79
$C_{19}H_{24}ONBr$. Calculated %: N 3.86

The oxalate, obtained by the mixing of solutions of the base and of anhydrous oxalic acid in absolute ether, melted at 218-220° (from 50% alcohol).

Found %: N 4.11; 4.26
$(C_{19}H_{23}ON)_2 \cdot (COOH)_2$. Calculated %: N 4.29.

The hydrochloride, hydrobromide, and oxalate of 2,5-dimethyl-1,4-diphenyl-4-piperidinol are insoluble in water.

2,5-Dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol (VIII)

Phenyllithium was prepared in the manner described above from lithium turnings (0.9 g), bromobenzene (11.5 g), and absolute ether (100 ml). The reaction was carried out in a stream of dry nitrogen. The flask containing the phenyllithium was cooled to −10°, and a solution of 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII) (10 g) of m.p. 71° in absolute ether (25 ml) was added dropwise. On the next day the dark-colored reaction mixture was heated for two hours at the boiling point of ether, and was then acidified with 10% hydrochloric acid at 0°. The oily precipitate that formed was separated and dissolved in warm concentrated hydrochloric acid. Neutral substances were removed by ether extraction. The free base was separated by the action of a 50% solution of caustic potash, and was extracted with ether. A stream of dry hydrogen chloride was passed through the dry ethereal solution of the base until it was saturated. The precipitated hydrochloride was washed with acetone and recrystallized from absolute alcohol, yielding 9.5 g of the monohydrochloride of 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol, m.p. 226.5-227.5°, in the form of glistening crystals, which were insoluble in water, but soluble in warm concentrated hydrochloric acid.

Found %: N 8.97; 9.17; Cl 11.48

$C_{18}H_{23}ON_2Cl$. Calculated %: N 8.78; Cl 11.13

The hydrochloride (m.p. 226.5-227.5°), when heated with a solution of caustic potash, yielded the free base, 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol (VIII) m.p. 112.5-114° (from a mixture of gasoline and acetone).

Found %: N 10.17; 9.96

$C_{18}H_{22}ON_2$. Calculated %: ·· N 9.92

Benzoic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α-form: R = C_6H_5)

Benzoyl chloride (15 ml) was added to 3.2 g of the hydrochloride of the low-melting 2,5-dimethyl-1-phenyl-4-piperidinol (II, α-form; m.p. 266-267°), and the mixture was heated at 130-145° for four hours. The excess of benzoyl chloride was driven off under reduced pressure, and the residue was crystallized from 50% alcohol, yielding 3 g of the water-insoluble benzoic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 217-218°.

Found %: N 4.34; 4.53

$C_{20}H_{24}O_2NCl$. Calculated %: N 4.05

The free base of the benzoic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = C_6H_5) was obtained by shaking the hydrochloride (m.p. 217-218°) with aqueous ammonia. Large crystals, m.p. 68-70° (from gasoline), were obtained.

Found %: N 4.83; 5.08

$C_{20}H_{23}O_2N$. Calculated %: N 4.53

Acetic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α form: R = CH_3)

a) A mixture of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°; 5 g) and acetic anhydride (50 ml) was saturated with dry hydrogen chloride and heated on a boiling water bath for four hours. The excess of acetic anhydride was removed under reduced pressure, and the residue was recrystallized from water, yielding 4 g of the hydrochloride of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 254-255°.

Found %: N 5.10; 4.93

$C_{15}H_{22}O_2NCl$. Calculated %: N 4.93

The free base of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = CH_3) was obtained in the usual way from the hydrochloride (m.p. 254-255°) in the form of colorless crystals, m.p. 84-85° (from gasoline).

Found %: N 5.77; 5.93

$C_{15}H_{21}O_2N$. Calculated %: N 5.67

b) A mixture of 2.5 g of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°) and 25 ml of acetyl chloride was boiled on a water bath for four hours. The excess of acetyl chloride was removed, and the residue was recrystallized from water, yielding 1.8 g of the above-described hydrochloride of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 254-255°.

Propionic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α-form: R= C_2H_5)

Propionic anhydride (10 ml) was added to a boiling mixture of 6.5 g of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°) and 35 ml of propionyl chloride until the precipitate present dissolved completely. The homogeneous reaction mixture was boiled for three hours. After removal under reduced pressure of the excess of propionyl chloride and propionic anhydride, the residue was recrystallized from ethyl methyl ketone, yielding 6.1 g of the hydrochloride of the propionic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = C_2H_5), m.p. 193-194°.

Found %: N 4.92; 4.77

$C_{16}H_{26}O_2NCl$. Calculated %: N 4.70

Benzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, β-form: R = C_6H_5)

The esterification was carried out by Spassow's method [2]. A solution of 7 g of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) in 30 ml of dry benzene was added to a mixture of benzoyl chloride (14 ml) and magnesium turnings (1.3 g). The reaction mixture was heated on a boiling water bath for three hours, and the excess of benzoyl chloride was then driven off under reduced pressure. The residue was diluted with water, neutralized with sodium carbonate, and extracted with ether. The product, after removal of ether, was vacuum-distilled, yielding 6 g of the benzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (high-melting form) (IX, R = C_6H_5), b.p. 160-165°/1 mm, which rapidly crystallized out, giving colorless crystals, m.p. 62.5-63.5° (from gasoline).

Found %: N 4.59; 4.79

$C_{20}H_{23}O_2N$. Calculated %: N 4.53

The hydrochloride of the benzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol was prepared by the action of dry hydrogen chloride on an ether solution of the base; it melted at 149-151° (from a mixture of ethyl methyl ketone and absolute alcohol).

Found %: N 4.05; 4.26

$C_{10}H_{24}O_2NCl$. Calculated %: N 4.05

On being dissolved in water, the hydrochloride was hydrolyzed with separation of the free base of the benzoic ester, (m.p. 62.5-63.5°).

Acetic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, β-form: R = CH_3)

The esterification was carried out by Spassow's method [2]. A solution of 4.1 g of the high-melting form of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) in 18 ml of dry benzene was added to a mixture of acetyl chloride (3.6 g) and magnesium turnings (0.6 g). The reaction was accompanied by evolution of heat, and the reaction mixture rapidly set into a crystalline mass. The product was diluted with water (20 ml), neutralized with sodium carbonate, and extracted with ether. The ether solution was dried with sodium sulfate, and the residue, after removal of ether, was vacuum-distilled, yielding 4.2 g of a substance of b.p. 135-138°/1 mm which was converted into its hydrochloride by saturating its ether solution with dry hydrogen chloride. The product (4.1 g) was the hydrochloride of the acetic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = CH_3), m.p. 180-181.5° (from a mixture of alcohol and ether).

Found %: N 4.97; 5.26

$C_{15}H_{22}O_2NCl$. Calculated %: N 4.93

p-Nitrobenzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, β-form: R = $C_6H_4NO_2$-p)

A solution of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) (14 g) in dry benzene (30 ml) was added to a mixture of p-nitrobenzoyl chloride (25 g), dissolved in 25 ml of benzene, and magnesium turnings (1.8 g). The reaction mixture was heated on a boiling water bath for six hours. On the next day the reaction product was treated with 18% hydrochloric acid, and the crystalline precipitate that separated was filtered off and washed with concentrated hydrochloric acid. The crude hydrochloride was recrystallized twice from a mixture of ethyl methyl ketone and absolute alcohol, yielding 19.5 g of the hydrochloride of the p-nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (high-melting form) in the form of fine colorless crystals, m.p. 195-196°.

Found %: N 7.07; 7 35

$C_{20}H_{23}O_4N_2Cl$. Calculated %: N 7.21

The hydrochloride was readily hydrolyzed by water with the formation of the free base of the p-nitrobenzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = $C_6H_4NO_2$-p) as a yellow powder of m.p. 130-131° (from gasoline).

Found %: N 8.16; 7.91

$C_{20}H_{22}O_4N_2$. Calculated %: N 7.90

p-Aminobenzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, β-form: R = $C_6H_4NH_2$-p)

The hydrochloride of the p-nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 195-196°; 11 g) was dissolved in warm 90% alcohol (130 ml) and hydrogenated in presence of a platinum catalyst prepared according to Adams. During the shaking, a part of the nitrobenzoic ester crystallized out in the flask, but as hydrogenation proceeded the whole of the precipitate went into solution. When 2120 ml (747 mm, 22°) of hydrogen had been absorbed, the catalyst was filtered off, alcohol was removed, under reduced pressure, and the residue was dissolved in water. The free base was precipitated from the aqueous solution by addition of 25% aqueous ammonia. Recrystallization from a mixture of gasoline and ethyl methyl ketone yielded 7 g of the p-aminobenzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = $C_6H_4NH_2$-p), m.p. 157-158°.

Found %: N 8.63; 8.53

$C_{20}H_{24}O_2N_2$. Calculated %: N 8.63

Acetic Ester of 4-Ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (X)

Acetyl chloride (10 ml) was added to 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 186-187°; 2.7 g). Acetic anhydride (3 ml) was added to the boiling reaction mixture in order to effect complete solution of the hydrochloride. The mixture was boiled on a water bath for five hours. The excess of acetyl chloride was distilled off, and the residue was crystallized from ethyl methyl ketone, yielding 2.5 g of the hydrochloride of the acetic ester of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol [the liquid stereoisomer (IV)] as long (25-30 mm) crystals, m.p. 182-183°.

Found %: N 4.77; 4.56

$C_{17}H_{26}O_2NCl$. Calculated %: N 4.49

In admixture with the original hydrochloride of the piperidinol it melted at 153-158°.

Benzoic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII: R = C_6H_5)

2,5-Dimethyl-1-phenyl-piperidone (20 g) dissolved in absolute ether (30 ml) was added dropwise over a period of one hour to a solution, cooled to −10° of phenyllithium, prepared from lithium turnings (2 g), bromobenzene (20 ml), and absolute ether (150 ml). The mixture was stirred at room temperature for two hours, and then at the boiling point of ether for 1 hr 30 min. The solution of O-lithium derivative so obtained was cooled with ice water, and a solution of freshly distilled benzoyl chloride (20 g) in absolute ether (30 ml) was added. On the next day the mixture was heated for four hours at the boil. The reaction product, after being cooled, was acidified with 10% hydrochloric acid, and the precipitate that formed was washed with hot 50% alcohol.

The product (25 g) was the hydrochloride of the benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (colorless crystals, insoluble in water), m.p. 187-188° (from a mixture of alcohol and benzene).

Found %: N 3.12; 3.30

$C_{26}H_{28}O_2NCl$. Calculated %: N 3.32

Shaking of the hydrochloride (m.p. 187-188°) with 25% aqueous ammonia yielded the free base of the benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII, R = C_6H_5) in the form of glistening plates, m.p. 178-179° (from petroleum ether).

Found %: N 3.89; 4.02

$C_{26}H_{27}O_2N$. Calculated %: N 3.64

Propionic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII: R = C_2H_5)

A solution of propionic anhydride (20 g) in absolute ether (30 ml) was added dropwise, under cooling with ice water and stirring, to a solution of the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, prepared as in the previous experiment from lithium turnings (2 g), bromobenzene (20 ml) and 2,5-dimethyl-1-phenyl-4-piperidone (18.5 g) in absolute ether (210 ml). The reaction mixture became thick and yellow. On the next day the mixture was boiled for four hours, and the reaction product was hydrolyzed with dilute hydrochloric acid (1:3). The precipitated crude hydrochloride was recrystallized from a mixture of alcohol and acetone, yielding 18 g of the hydrochloride of the propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, m.p. 167-168°, a substance of low solubility in water.

Found %: N 3.71; 3.80

$C_{22}H_{28}O_2NCl$. Calculated %: N 3.75

Treatment of the hydrochloride (m.p. 167-168°) with aqueous ammonia yielded the free base of the propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII, $R = C_2H_5$) in the form of large (8-12 mm) plates of m.p. 88-90° (from gasoline).

Found %: N 4.39; 4.49

$C_{22}H_{27}O_2N$. Calculated %: N 4.15

Acetic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII; $R = CH_3$)

A solution of acetic anhydride (20 ml) in absolute ether (30 ml) was added dropwise, under cooling with ice water and stirring, to a solution of the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, prepared from lithium turnings (2 g), bromobenzene (20 ml), 2,5-dimethyl-1-phenyl-4-piperidone (18 g), and absolute ether (200 ml). The further procedure was as above and yielded 16 g of the hydrochloride of the acetic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, m.p. 176-177.5° (from 60% alcohol), in the form of glistening needles of poor solubility in water.

Found %: N 3.76; 3.91

$C_{21}H_{26}O_2NCl$. Calculated %: N 3.89

SUMMARY

1. Reduction of 2,5-dimethyl-1-phenyl-4-piperidone (I) by sodium in moist ether, by sodium in alcohol, or by hydrogenation in presence of a platinum or nickel catalyst yields two stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidols (II).

2. Hydrogenation of the hydrochloride of 2,5-dimethyl-1-phenyl-4-piperidone in presence of a platinum catalyst gives only one stereoisomeric form, which corresponds to the low-melting form of the base (II, α-form).

3. A number of tertiary 4-piperidinols have been prepared by the action of alkylmagnesium halides and of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I) and on 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII). It has been established that in each case only one stereoisomeric form of the tertiary 4-piperidinol was formed.

4. By means of the condensation of 2,5-dimethyl-1-phenyl-4-piperidone with acetylene in presence of powdered caustic potash, the preparation has been effected in 50% yield of 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III), which was converted, by exhaustive hydrogenation, in the second stereoisomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV).

5. The syntheses have been carried out of esters of both isomeric forms of 2,5-dimethyl-1-phenyl-4-piperidinol with acetic, propionic, benzoic, p-nitrobenzoic, and p-aminobenzoic acids.

6. By means of various methods of esterification, the esters formed by 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol and by 2,5-dimethyl-1,4-diphenyl-4-piperidinol with acetic, propionic and benzoic acids have been prepared.

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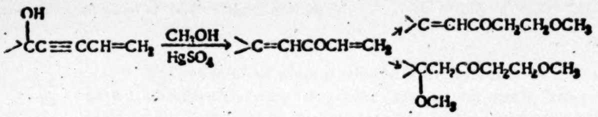
ACETYLENE DERIVATIVES

COMMUNICATION 149. SYNTHESIS OF β-AMINO KETONES BY THE ACTION OF SECONDARY AMINES ON β-METHOXY KETONES AND α,β-UNSATURATED KETONES

I. N. Nazarov and S. A. Vartanyan

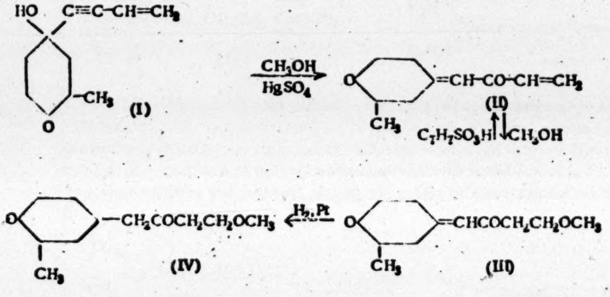
β-Amino ketones have recently found wide application for the synthesis of various physiologically active substances [1,2], and the development, therefore, of simple methods for their preparation may be of considerable importance for the further development of work directed to the discovery of new chemico-pharmaceutical and medicinal preparations.

As we have shown in a previous paper [3], β-methoxy ketones react readily with secondary amines with formation in high yield of the corresponding β-amino ketones, which may be prepared also by the direct addition of amines to α,β-unsaturated ketones. We have found in our laboratory that (vinylethynyl)-methanols readily isomerize under the influence of mercuric sulfate in methanol solution to give divinyl ketones, which, under the conditions of the experiment, combine with one or two molecules of methanol, yielding the corresponding β-methoxy ketones [4]:



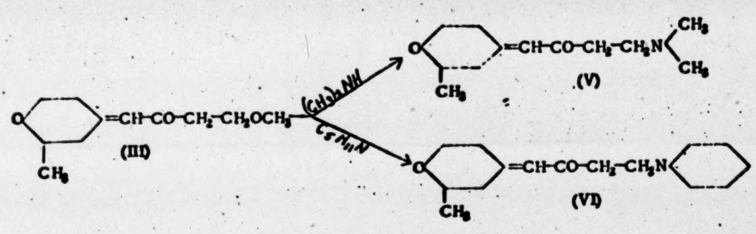
$$>\overset{OH}{C}C\equiv CCH=CH_2 \xrightarrow[HgSO_4]{CH_3OH} >C=CHCOCH=CH_2 \begin{cases} \to >C=CHCOCH_2CH_2OCH_3 \\ \to >\underset{OCH_3}{C}CH_2COCH_2CH_2OCH_3 \end{cases}$$

Continuing these investigations, we have now shown that tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol (I) also undergoes isomerization under the influence of mercuric sulfate in methanol solution, yielding the dienone II, which, under the conditions of the reaction, combines at the unsubstituted vinyl group with one molecule of methanol, forming the unsaturated methoxy ketone III. The free divinyl ketone (II) was prepared by vacuum distillation of the unsaturated methoxy ketone III in presence of p-toluenesulfonic acid [5]. The methoxy ketone III, when hydrogenated at a platinum catalyst, was converted into the saturated methoxy ketone IV. The structure of the methoxy ketone III was definitely proved by the aid of permanganate oxidation, which yielded 3-methoxypropionic acid and tetrahydro-2-methylpyran-4-one:

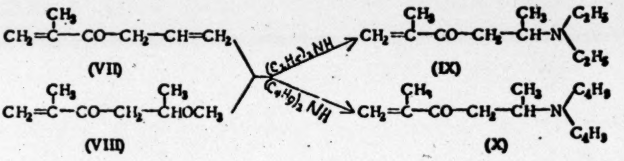


By the action of aqueous solutions of dimethylamine and of pyridine on the methoxy ketone III, the corresponding β-amino ketones V and VI were prepared: (See top of next page).

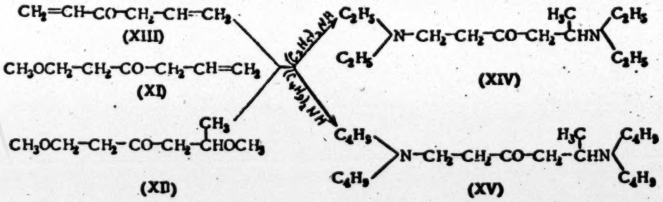
It was found that similar syntheses of amino ketones by the aid of diethyl- and dibutyl-amines did not go so smoothly and that it was better to obtain the required products by direct addition of these amines to α,β-unsaturated ketones, which are readily prepared by distillation of the corresponding β-methoxy ketones in presence of p-toluenesulfonic acid [5].



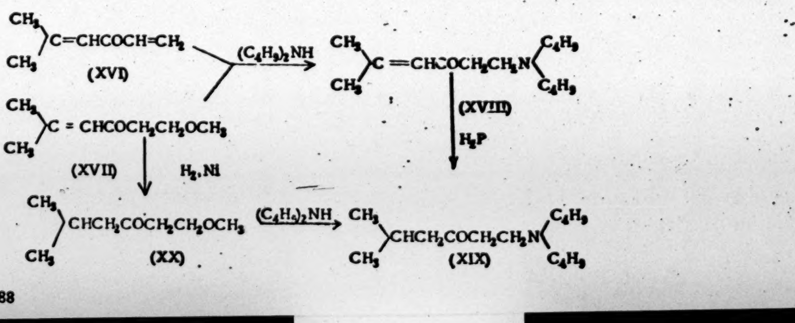
By the action of an aqueous solution of diethylamine on the methoxy ketone VIII [6], the synthesis was effected in poor yield of the amino ketone IX, which was obtained in good yield also by the direct addition of diethylamine to 2-methyl-1,5-hexadien-3-one (VII). In a similar way, the amino ketone X was prepared by the action of dibutylamine on the methoxy ketone VIII and by the direct addition of dibutylamine to the dienone VII:



The action of an aqueous solution of diethylamine on a mixture of the methoxy ketones XI and XII [7] gave 1,5-bis(diethylamino)-3-hexanone (XIV) in poor yield. The same diamino ketone was obtained in good yield by direct addition of diethylamine to 1,5-hexadien-3-one (XIII). This reaction went in a similar way when dibutylamine was used, and in this case 1,5-bis(dibutylamino)-3-hexanone (XV) was obtained:



When 5-methyl-1,4-hexadien-3-one (XVI) [5] and 1-methoxy-5-methyl-5-hexen-3-one (XVII) [4] were each treated with an aqueous solution of butylamine, the same amino ketone, 1-dibutylamino-5-methyl-4-hexen-3-one (XVIII), was obtained in each case, and when this was hydrogenated in presence of a platinum catalyst one molecule of hydrogen was absorbed with formation of 1-dibutylamino-5-methyl-3-hexanone (XIX). This amino ketone was prepared also by the action of dibutylamine on 1-methoxy-5-methyl-3-hexanone (XX) [8]:



It must be pointed out that, in the reactions of secondary amines with β-methoxy ketones, some volatile products were formed in all cases; they were not investigated. None of the amino ketones described in this paper gave a crystalline picrate: treatment with picric acid led to precipitation of a thick mass, which did not crystallize.

EXPERIMENTAL

Tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol (I) was prepared by the action of vinylethynylmagnesium bromide on tetrahydro-2-methylpyran-4-one, as previously described [9]. Distillation of the pyranol (I) was carried out in presence of pyrogallol (b.p. 100-102° at 4mm; n_D^{20} 1.5048).

Isomerization of Tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol

A mixture of the pyranol (I) (150 g), distilled methanol (370 g), and finely ground mercuric sulfate (3 g) was stirred for 8.5 hr at 35-40°. During this period, more mercuric sulfate was added (10 g, making 13 g in all). The reaction mixture was poured off the catalyst, neutralized with a solution of sodium carbonate, and extracted with ether; the extract was dried over sodium sulfate, repeated vacuum fractionation yielded the methoxy ketone (III) (80 g) in the form of a mobile liquid of characteristic odor; b.p. 109-111° at 1 mm; n_D^{20} 1.4800; d_4^{20} 1.0340; found MR 54.38; calculated MR 53.64.

Found %: C 66.19; 66.39; H 9.51; 9.77
$C_{11}H_{18}O_3$. Calculated %: C 66.66; H 9.20

Hydrogenation of the Methoxy Ketone (III)

Freshly distilled methoxy ketone (III) (b.p. 109-111° at 1 mm; n_D^{20} 1.4800) (3 g) was hydrogenated in ethanolic solution in presence of a platinum catalyst. The volume of hydrogen absorbed was 350 ml instead of 363 ml required by theory. The saturated methoxy ketone (IV) (2.3 g) was obtained in the form of a colorless, odorless liquid having b.p. 90-92° at 2 mm; n_D^{20} 1.4600; d_4^{20} 0.9987; found MR 54.33; calculated MR 54.09.

Found %: C 66.30; H 10.11
$C_{11}H_{22}O_3$. Calculated %: C 66.00; H 10.00

Oxidation of the Methoxy Ketone (III)

The methoxy ketone (III) (17 g) was mixed with water (200 ml), and to this mixture finely ground potassium permanganate (31 g) was added in small portions over a period of six hours under continuous stirring. The reaction mixture was set aside overnight, and stirring was continued on the next day for a further seven hours. Manganese dioxide was filtered off and washed with hot water; the neutral products were extracted with ether, and the extract was dried over sodium sulfate and vacuum distilled, yielding tetrahydro-2-methylpyran-4-one (b.p. 51-52° at 12 mm; n_D^{20} 1.4440), (4.2 g). Its semicarbazone melted at 169-170° and did not show depression with an authentic specimen [7]. The solution of salts was evaporated to dryness, decomposed with concentrated hydrochloric acid (20 ml), and carefully extracted with ether. After drying of the extract and removal of ether, the residue was vacuum-distilled, yielding 3-methoxypropionic acid, b.p. 100-103° at 12 mm; n_D^{20} 1.4200.

Preparation of the Dienone (II)

The methoxy ketone (III) (10 g) and p-toluenesulfonic acid (0.1 g) were introduced into a flask fitted with a fractionating column and heated at 100-110° at a pressure of 12 mm for 30 minutes. Methanol split off and the divinyl ketone slowly distilled over. Redistillation yielded the dienone (II) (5 g) as a yellow liquid having a sharp odor; b.p. 101-104° at 4 mm; n_D^{20} 1.4919; d_4^{20} 1.0050; found MR 47.98; calculated MR 46.90.

Found %: C 72.06; 72.01; H 8.79; 8.45
$C_{10}H_{14}O_2$. Calculated %: C 72.29; H 8.43

Preparation of the Amino Ketone (V)

A mixture of the methoxy ketone (III) (b.p. 109-111° at 1 mm; n_D^{20} 1.4800) and a 20% aqueous solution (50 g) of dimethylamine was heated in an autoclave at 80° for five hours. The excess of dimethylamine was removed under reduced pressure on a water bath at 45°. The solution was rendered slightly acid with hydrochloric acid and the neutral products were extracted with ether. The extract was dried with sodium sulfate and vacuum-distilled, yielding unchanged methoxy ketone (b.p. 109-112° at 1 mm; n_D^{20} 1.4810) (8.1 g).

The organic bases were salted out with potassium carbonate and extracted with ether. The ether extract was dried with sodium sulfate and vacuum-distilled, yielding the amino ketone (V) (6.3 g) as a thick liquid of characteristic amine odor, which yellowed on standing; b.p. 128-130° at 4 mm; n_D^{20} 1.5040; d_4^{20} 1.0370; found MR 60.30; calculated MR 59.85.

Found %: N 6.83; 6.64
$C_{12}H_{21}O_2N$. Calculated %: N 6.63

Preparation of the Amino Ketone (VI)

Piperidine (10 g) and water (3 g) were added to the methoxy ketone (III) (12 g). When the water was added the temperature rose to 45°. The mixture was heated at 80° for three hours and was then treated as in the previous experiment. The product was the amino ketone (VI), b.p. 138-140° at 4 mm; n_D^{20} 1.5150; d_4^{20} 1.0440; found MR 72.68; calculated MR 72.20.

Found %: N 5.20; 5.19
$C_{15}H_{25}O_2N$. Calculated %: N 5.57

Preparation of the Amino Ketone (IX)

a) Diethylamine (10 g) was added dropwise to 2-methyl-1,5-hexadien-3-one (VII) (b.p. 80-83° at 80 mm; n_D^{20} 1.4713) (15 g) [6]. the temperature of the mixture was found to rise to 65°. The mixture was then heated in a glass ampoule at 80° for three hours and was then treated as in the preceding experiments. The ether solution of the organic base was dried over magnesium sulfate, and the product was vacuum-distilled, yielding 5-diethylamino-2-methyl-1-hexen-3-one (IX) as a clear liquid of characteristic odor that yellowed on standing; b.p. 94-95° at 7 mm; n_D^{20} 1.4580; d_4^{20} 0.8821; found MR 56.62; calculated MR 56.40.

Found %: N 8.07
$C_{11}H_{21}ON$. Calculated %: N 7.65

b) 5-Methoxy-2-methyl-1-hexen-3-one (VIII) (b.p. 56-59° at 6 mm; n_D^{20} 1.4400) (15 g) [6]. diethylamine (15 g), and water (5 g) were heated together in a glass ampoule at 60° for two hours and then treated in the usual way. The ether solution of the organic base was dried with magnesium sulfate, and the product was vacuum-distilled, yielding the above-described 5-diethylamino-2-methyl-1-hexen-3-one (IX), b.p. 109-112° at 10 mm; n_D^{20} 1.4580.

Preparation of the Amino Ketone (X)

a) Dibutylamine (11 g) was added dropwise to 2-methyl-1,5-hexadien-3-one (VII) (b.p. 80-83° at 80 mm; n_D^{20} 1.4710) (15 g); the temperature of the mixture was observed to rise to 45°. The mixture was heated at 80° for six hours and then treated in the usual way, yielding 5-dibutylamino-2-methyl-1-hexen-3-one (X); b.p. 110-112° at 3 mm; n_4^{20} 1.4620; d_D^{20} 0.8740; found MR 75.46; calculated MR 74.95.

Found %: N 6.27; 5.93
$C_{15}H_{29}ON$. Calculated %: N 5.84

b) A mixture of 5-methoxy-2-methyl-1-hexen-3-one (VIII) (b.p. 56-59° at 6 mm; n_D^{20} 1.4400)(10 g), dibutylamine (10 g)and water (2 g) was heated in a glass ampoule for three hours at 60°. The usual treatment yielded 1.3 g of the amine ketone (X), b.p. 111-113° at 2 mm; n_D^{20} 1.4620.

Preparation of the Diamino Ketone (XIV)

a) Diethylamine (16 g) was added dropwise to 1,5-hexadien-3-one (XIII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4729) (10 g) [7]. The temperature of the reaction mixture rose to 65°, and the mixture was heated in a glass ampoule for three hours at 70° and was then vacuum-fractionated, yielding 1,5-bis(diethylamino)-3-hexanone (XIV) (18.5 g) as a clear liquid that yellowed on standing; b.p. 94-95° at 5 mm; n_D^{20} 1.4630; d_4^{20} 0.8924; found MR 74.68; calculated MR 74.77.

Found %: N 11.46
$C_{14}H_{30}ON_2$. Calculated %: N 11.57

b) The mixture of methoxy ketones (XI and XII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4330) (10 g) [7] was heated together with diethylamine (10 g) and water (2 g) at 60° for four hours. The excess of diethylamine was driven off under reduced pressure on a water bath at 45°. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding the above-described 1,5-bis(diethylamino)-3-hexanone (XIV) (1.7 g); b.p. 96-98° at 8 mm; n_D^{20} 1.4628.

Preparation of the Diamino Ketone (XV)

a) Dibutylamine (18 g) was added to 1,5-hexadien-3-one (XIII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4730) (10 g), and the temperature of the reaction mixture rose to 67°. When the dibutylamine had been added, the reaction mixture was heated in a glass ampoule for one hour at 70°, and was then vacuum-fractionated, yielding 1,5-bis(dibutylamino)-3-hexanone (XV) (17.3 g) as a clear liquid, b.p. 110-111° at 1 mm; n_D^{20} 1.4620; d_4^{20} 0.8680; found MR 112.10, calculated MR 111.73.

Found %: N 8.21; 8.04
$C_{22}H_{46}ON_2$. Calculated %: N 7.91

b) A mixture of the methoxy ketones (XI) and (XII) (b.p. 85-89° at 9 mm; n_D^{20} 1.4330),(20 g) was heated with dibutylamine (20 g) and water (4 g) in a glass ampoule for six hours at 65°. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The solution was slightly acidified with hydrochloric acid, and the neutral products were extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 11 g of unchanged methoxy ketones, b.p. 84-86° at 9 mm, n_D^{20} 1.4300. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-fractionated, yielding 2.5 g of the above-described amino ketone (XV), b.p. 107-109° at 7 mm; n_D^{20} 1.4620.

Preparation of the Amino Ketone (XVIII)

a) Dibutylamine (13 g) was added to 5-methyl-1,4-hexadien-3-one (XVI) (b.p. 70-73° at 70 mm; n_D^{20} 1.4740) (10 g) [5], and the temperature of the mixture rose to 70°. The mixture was then heated at 80° in a glass ampoule for 30 minutes. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The reaction mixture was slightly acidified with hydrochloric acid and extracted with ether in order to remove neutral products, which, however, were almost absent (1 g). The organic base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 12.5 g of 1-dibutylamino-5-methyl-4-hexen-3-one (XVIII), b.p. 123-125° at 4 mm; n_D^{20} 1.4600; d_4^{20} 0.8730; found MR 75.00; calculated MR 74.95.

Found %: N 6.01
$C_{15}H_{29}ON$. Calculated %: N 5.84

b) A mixture of 1-methoxy-5-methyl-4-hexen-3-one (b.p. 80-82° at 10 mm; n_D^{20} 1.4570) (15 g) [4], dibutylamine (11 g), and water (3 g) was heated in a glass ampoule for four hours at 80° and the reaction mixture was treated as in the previous experiment, yielding 2.1 g of the amino ketone (XVIII), b.p. 127-129° at 5 mm; n_D^{20} 1.4602.

Preparation of the Amino Ketone (XIX)

a) Freshly distilled amino ketone (XVIII) (4 g) was dissolved in alcohol (15 ml) and hydrogenated in presence of a platinum catalyst for eight hours. The volume of hydrogen absorbed was 430 ml, instead of the theoretically required 400 ml. The catalyst was filtered off, the alcohol was driven off, and vacuum fractionation of the residue yielded 1.9 g of 1-dibutylamino-5-methyl-3-hexanone (XIX), b.p. 102-103° at 2 mm; n_D^{20} 1.4500; d_4^{20} 0.8553; found MR 75.65; calculated MR 75.42.

Found %: N 5.32; 6.01
$C_{15}H_{31}ON$. Calculated %: N 5.80

b) Dibutylamine (7 g) and water (3 g) were added to 1-methoxy-5-methyl-3-hexanone (XX) (b.p. 64° at 11 mm; n_D^{20} 1.4190) (8 g) [8], and the mixture was heated in a glass ampoule at 80° for 2 hr 30 min. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The solution was slightly acidified with hydrochloric acid, and the neutral products were extracted with ether. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 3.7 g of the above-described amino ketone (XIX); b.p. 101-103° at 2 mm; n_D^{20} 1.4500.

SUMMARY

1. Under the influence of mercuric sulfate in methanol solution, tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol (I) isomerizes into the divinyl ketone (II). The latter, under the conditions of the reaction unites

with methanol and gives the methoxy ketone (III), which, on hydrogenation, absorbs one molecule of hydrogen, yielding the saturated methoxy ketone (IV).

2. When methanol is caused to split from the unsaturated methoxy ketone (III), the divinyl ketone (II) is obtained in good yield.

3. By the action of aqueous solutions of dimethylamine and piperidine on the methoxy ketone (III), the amino ketones (V) and (VI) respectively are obtained.

4. By the action of diethylamine (or dibutylamine) on the ketone (VII) or the ketone (VIII), the amino ketone (IX) or (X) is formed.

5. By the action of diethylamine (or dibutylamine) on the ketones (XI), (XII), or (XIII), the diamino ketone (XIV) or (XV) is formed.

6. By the action of dibutylamine on the ketone (XVI) or the ketone (XVII), the amino ketone (XVIII) is obtained, and this, on being hydrogenated, absorbs one molecule of hydrogen and forms the saturated amino ketone (XIX), which is obtained also by the action of dibutylamine on the saturated methoxy ketone (XX).

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• See Consultants Bureau English translation, page 1833.
•• See Consultants Bureau English translation, page 1643.
••• See Consultants Bureau English translation, page 413.

SYSTEMATICS OF MACROMOLECULAR COMPOUNDS

(NOMENCLATURE AND CLASSIFICATION OF MACROMOLECULAR COMPOUNDS)*

V. V. Korshak

Only in the last two decades has the chemistry of macromolecular compounds become a separate entity and taken shape as a section among other sections of organic chemistry. Being an independent branch of science, it is characterized, when compared with other sections of organic chemistry, by its much greater use of the methods of physics, and also of physical and colloid chemistry, for it constitutes in essence a synthesis of these sciences, among which the leading role is to be assigned to organic chemistry.

However, as the subject and field of the chemistry of macromolecular compounds are of such recent development, a number of fundamental questions determining its further progress have not yet been solved. Among such questions of a purely chemical character, the problem of the systematics of macromolecular compounds takes first place. The primary importance of dealing with problems of systematics results from the fact that work on the synthesis of new compounds can now no longer be based on those empirical principles that have hitherto prevailed. For further progress in this field it is essential to systematize and analyze the abundance of material that chemists have now accumulated. Only on this basis can further planned progress in the synthetic chemistry of high polymers be made. In this connection there is the question of the need for dealing with such preliminary problems as the nomenclature and classification of macromolecular compounds.

Nomenclature of Macromolecular Compounds

The names of macromolecular compounds have been formed hitherto in an unsystematic fashion. Natural compounds generally have their own names, which do not in any way reflect their structures. Examples are cellulose, starch, protein, inulin, lignin, etc.

Synthetic compounds are generally named after the starting substances from which they are obtained. Thus, all polymers are named after the starting substance, with the addition only of the prefix "poly", e.g. polyethylene, polystyrene, polyvinyl chloride, etc. In the case of polycondensation products, the word "resin" is added to the names of the starting substances, e.g. phenol – formaldehyde resin, urea – formaldehyde resin, melamine – formaldehyde resin, etc. As will be seen, in the majority of cases these names do not at all reflect the chemical structure of the macromolecular compound itself and therefore do not give any idea of the possible chemical reactions of the substance, and therefore of its properties.

Also, one and the same compound may have several names, corresponding to various starting substances from which it may be prepared. Thus, polyethylene oxide (the polymer of ethylene oxide) is called polyethylene glycol, if it is obtained from glycol. Polycaprolactam, obtained by the polymerization of caprolactam, may be obtained also by the polycondensation of aminocaproic acid, and should then be called polycaproamide. The number of examples of this sort will, of course, grow ever greater as time goes on. This is a further proof of the need for a nomenclature that is based in the first place on the structure of the macromolecular compound itself, and not on various preparative methods, the number of which may be fairly high.

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* Printed in accordance with the resolution of the Seventh All-Union Conference on Macromolecular Compounds, which took place in Moscow on June 12th, 1952. The basic principles of the proposed systematic scheme were reported at the Sixth All-Union Conference on Macromolecular Compounds, held June 21-25th, 1949 in Leningrad, and were published in a number of monographs [1,2,3] and articles [4,5].

The Seventh All-Union Conference on Macromolecular Compounds approved in principle the nomenclature and classification of macromolecular compounds published here, and the Conference resolved that it should be published in order that it might be discussed and that greater precision might be given to the basic ideas.

(NOTE: In view of the nature of this paper, the author's nomenclature is transcribed as closely as possible, i.e. is not adjusted to American practice, as in the remaining papers of this issue. — Publisher).

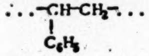
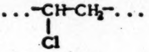
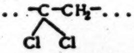
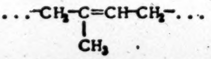
The great need for a nomenclature based on chemical principles is generally recognized, a proof of which may be found in the appearance in 1952 of a new nomenclature, drawn up by a group of foreign chemists [6]. It must be pointed out, however, that, apart from their proposals relating to terms characterizing the physical properties of the polymers and their viscosity in solution, many of their proposed terms cannot be regarded as satisfactory, and this is particularly true of the chemical terminology of high polymers. Hence, the appearance of this nomenclature does not prompt us to withdraw the nomenclature for the naming of macromolecular compounds proposed by us considerably earlier (1949), which is expounded below.

The basis of our proposed rational nomenclature is the structure of the main chain of the macromolecule. The prefix "poly" will indicate that we have the name of a macromolecular compound. After the prefix will be placed a bracket, after which will be given the number and disposition of substituents; after each will be indicated the percent content, which is of importance in copolymers. In parentheses will be given the name of the fundamental repeating unit of the macromolecule chain[*]

Examples of the names of a number of polymers are given below in Table 1.

TABLE 1

Examples of the Rational Names of Polymers

Formula	Name of polymer	
	Usual	Rational
$\ldots-CH_2-\ldots$	Polyethylene	Poly(methylene)
 $\ldots-\underset{C_6H_5}{\underset{\vert}{C}H}-CH_2-\ldots$	Polystyrene	Poly[phenyl(ethylene)]
 $\ldots-\underset{Cl}{\underset{\vert}{C}H}-CH_2-\ldots$	Polyvinyl chloride	Poly[chloro(ethylene)]
 $\ldots-\underset{Cl\quad Cl}{C}-CH_2-\ldots$	Polyvinylidene chloride	Poly[1,1-dichloro(ethylene)]
 $\ldots-CH_2-\underset{CH_3}{\underset{\vert}{C}}=CH-CH_2-\ldots$	Rubber	Poly[2-methyl(buten-2-ylene-1,4)]
$\ldots-NH(CH_2)_5CO-\ldots$	Polycaprolactam	Poly[amino-1-caproylene-1,7]
$\ldots-O(CH_2)_2-\ldots$	Polyethylene oxide	Poly(hydroxyethylene)

We shall confine ourselves to these examples, which illustrate sufficiently clearly the principles of this nomenclature. The names of a large number of polymers will be given later in Tables 2-6, when describing the classification of macromolecular compounds.

It must be made clear, however, that the use of rational names in no way excludes the use of the common names of polymers that are already a part of chemical language. Trivial names often have the advantage of greater brevity, particularly in the case of natural compounds for the naming of compounds such as cellulose, protein, lignin, inulin, etc., and this alone justifies their further use. There are names in use, however, which are contrary to all principles of chemical nomenclature and should no longer be used, being completely incorrect. Examples of such names are "polychlorovinyl", "polychlorovinylidene", "perchlorovinyl", etc. These names must be replaced, respectively, by polyvinyl chloride, polyvinylidene chloride, chlorinated polyvinyl chloride, etc., or by the corresponding rational names: poly[chloro(ethylene)], poly[1,1-dichloro(ethylene)], etc.

In our examination of classification, we shall use these rational names in addition to generally accepted names.

Classification of Macromolecular Compounds

Questions relating to the classification of macromolecular compounds have been considered by many chemists.

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[*] There is as yet no consistent nomenclature for bivalent radicals. By analogy with ethylene we form their names by addition of the ending "ylene".

Thus, Carothers [7] divided them into two classes:

1. Polymers of the additive type, or A-polymers. This class comprises substances for which the formula of the monomer is identical with the formula of the structural unit of the polymer. In this class be placed: polyolefins, polyoxymethylenes, polystyrenes, rubber, etc.

2. Polymers of the condensation type, or C-polymers. In this class the composition of the monomer is not identical with that of the structural unit of the polymer. This class includes esters of polyhydric alcohols with polybasic acids, phenol-aldehyde resins, urea-aldehyde resins, etc.

Kienle [8] took the behavior of synthetic resins when heated or treated with reagents as the basis of his classification; he distinguished three groups:

1. Thermoreactive resins. These are resins that are converted by heat into an infusible condition; they include resins based on glycerol and polybasic acids, acetylene derivatives, polyolefin resins, phenol- and urea-aldehyde resins, etc.

2. Thermoplastic resins. These are resins that do not change on being heated and do not lose their plastic properties; they include polystyrene, polyvinyl acetate, polyethylene, condensation products formed by glycols with dicarboxylic acids, etc.

3. Element-reactive resins. These are resins that go into an infusible condition under the action of elements such as oxygen or sulfur. This group includes resins prepared from glycerol and polybasic acids together with drying oils, sulfur-olefin resins, etc.

Morgan, Megson, and Holmes [9] divide these compounds into two groups:

1. Condensation resins, which solidify, being converted into infusible, insoluble products.

2. Polymerization resins, the polymerization products from unsaturated compounds; they are not able to go into an infusible condition.

Petrov, Rutovsky, and Losev [10] take the chemical reactions used in the preparation of synthetic resins as their basis and divide them into the following groups:

1. Plastics based on condensation products (phenol- and urea-aldehyde, polyamide resins).

2. Plastics based on polymerization products (polystyrene, polyethylene, etc).

3. Plastics based on esters and ethers of cellulose.

4. Plastics based on proteins.

5. Plastics based on natural and artificial bitumins.

6. Plastics based on the oxidation products of the glycerides of unsaturated fatty acids.

Fischer [11] divides all synthetic polymers into two groups: elastomers and plastomers. Elastomers are subdivided into:

1. Elastoprenes (polybutadiene, polyisoprene, etc.).

2. Elastolenes (polyisobutene).

3. Elastothiomers (thiokols).

4. Elastoplastics (polyacrylates, polyvinyl acetate, etc.).

Plastomers are subdivided into:

1. True thermoplastics (shellac, polystyrene, celluloid, etc.).

2. Plastics that solidify when heated (phenol-formaldehyde resins, glyptals, etc.).

Meyer [12] divides all macromolecular compounds into the following seven groups:

1. Inorganic high polymers (sulfur, selenium, graphite, diamond, silicon, boron, silica, polyphosphonitrile chloride, glass, etc.).

2. Macromolecular hydrocarbons (polyvinyl esters, alcohols, acids, polystyrene, rubber, chloroprene, etc.).

3. Polymeric ethers, sulfides, etc. (polyoxymethylenes, polyethylene oxide, glyptals, polysulfides, polyamides, phenol-formaldehyde, urea-formaldehyde, and aldehyde resins, etc.).

4. Cellulose and its derivatives.

5. Substances associated with cellulose (lignin, gums, etc.).

6. Starch.

7. Proteins.

Staudinger [13] classified organic compounds according to molecular weight and number of carbon atoms in the molecule into a number of groups, which are given in Table 2.

TABLE 2

Staudinger's Classification of Organic Compounds

Substances	Molecular weight	No. of carbon atoms in molecule
A. Low-molecular-weight organic compounds; completely homogeneous substances	16-5000	1-500
B. "The world of every-day molecules"; polymeric and constitutionally homologous substances:		
1. Semicolloids	1000-10000	100-1000
2. Eucolloids	10^4–10^6	10^3–10^5
3. Macromolecular insoluble substances	10^4–10^x	10^3–10^{x-1}
4. Diamond (1 g)	$6.06 \cdot 10^{23}$	$5 \cdot 10^{22}$

In this way he divided all organic compounds into two groups (low- and high-molecular-weight compounds). The first group contains those which can be obtained in a pure, homogeneous state, and the second group contains those which are built up of macromolecules and can be obtained only in polymerically homogeneous state, i.e. as a mixture of polymer-homologs. The macromolecular substances are divided in their turn into four groups: semicolloids, eucolloids, insoluble substances, and three-dimensional substances. At the basis of this subdivision lies the solubility of the substance and the properties of its solution. Semicolloids are readily powdered substances that dissolve without swelling; their dilute solutions are of low viscosity and obey the Hagen-Poiseuille law.

Eucolloids are solid substances that swell before dissolving; their solutions are very viscous and behave abnormally during efflux. The molecules of eucolloids have chain lengths of greater than 3000 A. Insoluble macromolecular substances have longer chains (1,000,000 A and greater) and are therefore unable to go into solution. Three-dimensional macromolecular substances, the most typical example of which is diamond, are also insoluble, but from another cause: their crystal lattices extend in space owing to the fact that individual chains are firmly attached to one another by a large number of cross links and cannot be separated without rupture of these links.

Staudinger made a further subdivision of the group of soluble macromolecular substances into three groups: homopolar, heteropolar, and coordination compounds. The first contains rubber, polystyrene, cellulose acetate, and similar neutral substances. The second contains the phosphonium salts of rubber, which contain a macromolecular cation, and also sodium polyacrylate and complex compounds formed by cellulose with the cuprammonium salt in Schweizer's solution, which contain macromolecular anions. To this group also belong the proteins, which are amphoteric macromolecular compounds. To the coordination group he assigns polyvinyl alcohol, polyacrylic acid, cellulose, starch, lichenin, and other similar compounds.

Apart from these, many more classifications have been proposed based on a great variety of criteria [14].

This short survey shows that the abundance of proposed variants, while undoubtedly indicating that the need for correct classification is widely felt, is at the same time an indication that the proposed methods are not regarded as wholly satisfactory.

It is, in fact, true that, at the present time, a large number of investigations, aimed at the discovery of new macromolecular substances, the elucidation of their structures, and the study of their properties, are providing an enormous amount of material that has not yet been systematized within any definite plan. The literature on macromolecular compounds regards and classifies these compounds, as we have seen, on the basis of casual and mainly arbitrary criteria, such as their origin, the starting substances, their physical properties, etc.

The attempts at generalization that have taken place up to the present time have generally related to particular narrow classes, such as vinyl compounds, cellulose, rubber, etc., and have thus not brought any order into the whole enormous field of macromolecular compounds, which comprises a great accumulation of experimental material, which is linked together only in a casual way.

It is quite clear that for a classification of macromolecular compounds to be fruitful and useful, its basis must rest on an invariable criterion, such as the structure of the macromolecular compound itself. Only then can a system be created that will correctly portray the interrelations of already known macromolecular substances, make it possible to predict new compounds, and so act as a leading thread in scientific investigations. All other methods of coordinating macromolecular substances, based on classification by starting substances, by methods of preparation, etc., can have only subsidiary significance. Directed by these considerations, we made an attempt to make a system of classification of macromolecular compounds having as its basis the structure of the actual chain, which in the case of high polymers may be equivalent to the structure of the essential repeating units of which the chain of the macromolecule is built up.

Principles of the Chemical Classification of Macromolecular Compounds

At the basis of the classification of macromolecular compounds we place the structure of the main chain, and also the presence of substituents, their number, nature, and disposition. All macromolecular compounds can then be grouped into two large classes:

1. Substances having chains that are built up from the atoms of one element only (homochain compounds). When the element is carbon, they will be *carbochain compounds*; when it is sulfur, they will be sulfidochain compounds, when it is arsenic they will be arsenochain compounds, and so on. Examples of carbochain compounds are polymerization products from unsaturated compounds, such as rubber, polyvinyl chloride, polyethylene, etc.

2. Substances having chains that include atoms of carbon, oxygen, nitrogen, sulfur, silicon, and other elements. This class we shall call *heterochain compounds*. Examples of compounds of this class are thiokol, cellulose, proteins, organosilicon polymers, etc.

The distinction between these classes appears most clearly in their chemical properties, particularly in the resistance of compounds of the first class to hydrolysis and the tendency of substances of the second class to be destroyed by hydrolyzing agents. Each of these main classes can be subdivided into groups according to the structure of the chain, the presence of double bonds in the chain, and, in the case of the second class, on the number and nature of the hetero atoms. Thus, in the first class, carbochain compounds, we shall have the following groups:

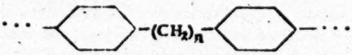
1. Polymethylene group

$$\ldots-CH_2-CH_2-CH_2-CH_2-\ldots$$

2. Unsaturated chain group

$$\ldots-CH_2-CH_2{=}CH-CH_2-\ldots$$

3. Cyclochain group



In the second class we shall have the following groups:

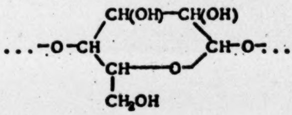
1. Oxygen-containing chains (polyethers)

$$\ldots-CH_2-O-CH_2-O-CH_2-O-\ldots \text{ etc.}$$
$$\ldots-(CH_2)_n-CO-O(CH_2)_m-CO-O-\ldots \text{ etc.}$$

2. Nitrogen-containing chains (structure analogous to preceding).

3. Sulfur-containing chains (structure analogous to first group).

4. Ring- and oxygen-containing chains (cellulose, starch, etc.).



Each of these groups is divided in its turn into subgroups according to what side groups are present, their nature, number, disposition, etc.; for example, the first group of the carbochain class will contain the following subgroups:

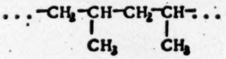
a) halogen compounds

$$\ldots-CH_2-CHCl-CH_2-CHCl-\ldots$$

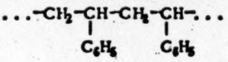
b) hydroxy compounds

$$\ldots-CH_2-CH(OH)-CH_2-CH(OH)-\ldots$$

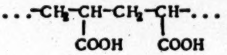
c) compounds having side chains of various structures



$$\ldots-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\ldots$$



$$\ldots-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-\ldots$$



$$\ldots-CH_2-\underset{COOH}{\underset{|}{CH}}-CH_2-\underset{COOH}{\underset{|}{CH}}-\ldots$$

These examples give a sufficiently clear illustration of the basic elements of the proposed system for the classification of macromolecular compounds.

An essential element that must appear in the system is the quantitative characterization: the "degree of substitution", which indicates the number of substituents in the chain calculated for a definite number of carbon atoms (for example, 100); we shall represent it by the index "d_s". This index may change within wide limits: from 0 for polyethylene to 100 for polytetrafluoroethylene. This index can be applied usefully also to the case of copolymers. For heterochain compounds it is expedient to introduce the concept of "heterochain characteristic", which will be denoted by the index "h_c" and which indicates the number of hetero atoms per 100 atoms in the chain. This index is 100 for thiokol, 50 for formaldehyde polymers, 33 for the polymer of ethylene oxide, and so on.

Below we give the basis of the scheme for the chemical classification of macromolecular compounds.

A. Carbochain Compounds

We shall give the name of carbochain compounds to all macromolecular compounds in which the macromolecule chain is composed only of carbon atoms, and so distinguish them from heterochain compounds, in which the chain contains also hetero atoms (oxygen, nitrogen, sulfur, etc.). Carbochain compounds constitute a large class of macromolecular compounds, the numerous members of which contain a great variety of substituents. In this class are found compounds, such as natural and various forms of synthetic rubber, polystyrene, polyvinyl chloride, and many others, which are widely applied in various branches of industry.

The principal method for the preparation of carbochain compounds consists in the polymerization of unsaturated hydrocarbons or their derivatives occurring by way of the opening of double bonds and formation of the straight chain of the macromolecule:

$$xCH_2=CHX \longrightarrow (-CH_2-CHX-)_x.$$

Certain carbochain compounds may be obtained also by a polycondensation reaction from dihalo derivatives by the action of alkali metals:

$$x\,BrRBr + 2xNa \longrightarrow 2xNaBr + (R)_x.$$

TABLE 3

Saturated Carbochain Macromolecular Compounds

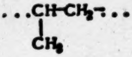
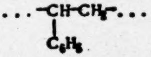
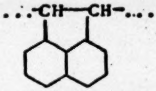
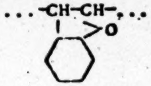
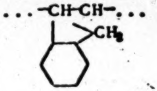
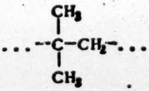
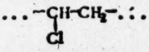
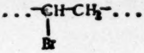
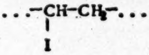
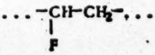
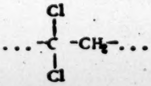
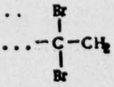
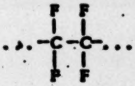
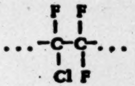
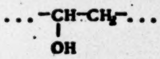
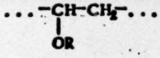
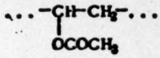
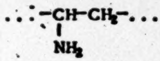
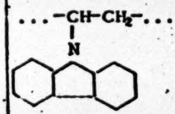
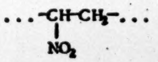
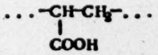
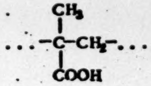
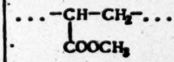
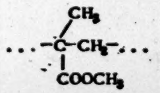
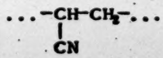
Group	Subgroup	Example		
		Name		Formula
		rational	usual	
1	2	3	4	5
Hydrocarbons	No substituent	Poly(methylene)	Polyethylene	$\ldots-CH_2-CH_2-\ldots$
"	Monoalkyl-substd.	Poly[1-methyl(ethylene)]	Polypropylene	 $\ldots CH(CH_3)-CH_2-\ldots$
"	Monoaryl-substd.	Poly[1-phenyl(ethylene)]	Polystyrene	 $\ldots-CH(C_6H_5)-CH_2-\ldots$
"	"	Poly[naphthylene-(ethylene)]	Polyacenaphthene	
"	"	Poly[phenyleneoxy-(ethylene)]	Polycoumarone	
"	"	Poly[benzylene(ethylene)]	Polyindene	
"	Dialkylsubstd.	Poly[1,1-dimethyl-(ethylene)	Polyisobutylene	 $\ldots-C(CH_3)_2-CH_2-\ldots$
Halosubstd.	Monohalo-substd.	Poly[chloro(ethylene)]	Polyvinyl chloride	 $\ldots-CH(Cl)-CH_2-\ldots$
"	"	Poly[bromo(ethylene)]	Polyvinyl bromide	 $\ldots-CH(Br)-CH_2-\ldots$
"	"	Poly[iodo(ethylene)]	Polyvinyl iodide	 $\ldots-CH(I)-CH_2-\ldots$
"	"	Poly[fluoro(ethylene)]	Polyvinyl fluoride	 $\ldots-CH(F)-CH_2-\ldots$
"	Dihalosubstd.	Poly[1,1-dichloro-(ethylene)]	Polyvinylidene chloride	 $\ldots-CCl_2-CH_2-\ldots$
"	"	Poly[1,1-dibromo-(ethylene)]	Polyvinylidene bromide	 $\ldots-CBr_2-CH_2$

TABLE 3 — (Continued)

Group	Subgroup	Example		
		Name		
		rational	usual	Formula
Halosubstd.	Tetrahalo-substd.	Poly[tetrafluoro-(ethylene)]	Teflon	 $\cdots-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\cdots$
"	"	Poly[trifluorochloro-(ethylene)]	Polytrifluorochloroethylene	 $\cdots-\overset{F}{\underset{Cl}{C}}-\overset{F}{\underset{F}{C}}-\cdots$
Alcohols	Monohydric alcohols	Poly[hydroxy(ethylene)]	Polyvinyl alcohol	 $\cdots-\underset{OH}{CH}-CH_2-\cdots$
Ethers	Monoalkyl ethers	Poly[alkoxy(ethylene)]	Polyvinyl alkyl ether	 $\cdots-\underset{OR}{CH}-CH_2-\cdots$
Esters	Monocarboxylic-esters	Poly[acetoxy(ethylene)]	Polyvinyl acetate	 $\cdots-\underset{OCOCH_3}{CH}-CH_2-\cdots$
Amines	Monoamines	Poly[amino(ethylene)]	Polyvinylamine	 $\cdots-\underset{NH_2}{CH}-CH_2-\cdots$
"	"	Poly[carbazolyl(ethylene)]	Polyvinylcarbazole	
Nitro Compound	Mononitro Compounds	Poly[nitro(ethylene)]	Polynitroethylene	 $\cdots-\underset{NO_2}{CH}-CH_2-\cdots$
Carboxylic acids	Monocarboxylic acids	Poly[carboxy(ethylene)]	Polyacrylic acid	 $\cdots-\underset{COOH}{CH}-CH_2-\cdots$
"	"	Poly[1-methyl-1-carboxy-(ethylene)]	Polymethacrylic acid	 $\cdots-\overset{CH_3}{\underset{COOH}{C}}-CH_2-\cdots$
Carboxylic esters	Monocarboxylic esters	Poly[carboxymethyl-(ethylene)]	Polymethyl acrylate	 $\cdots-\underset{COOCH_3}{CH}-CH_2-\cdots$
"	"	Poly[1-methyl-1-carboxy-methyl(ethylene)]	Polymethyl methacrylate	 $\cdots-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\cdots$
Nitriles	Mononitriles	Poly[cyano(ethylene)]	Polyacrylonitrile	 $\cdots-\underset{CN}{CH}-CH_2-\cdots$

A third method for the preparation of carbochain compounds consists in the polymerization of bivalent free radicals. This method is still quite new and has been developed only in its application to the case of the preparation of polymethylene by the polymerization of methylene radicals:

$$xCH_2 \longrightarrow (-CH_2-)_x.$$

In this case the methylene radicals are obtained by the decomposition of diazomethane or by the reduction of carbon monoxide.

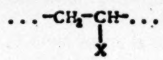
In the future, no doubt, when methods for the preparation of the necessary free radicals have become more perfect, this method will receive wide development.

According to the structure of the carbon chain, carbochain compounds may be divided into three groups:

A. compounds having a saturated chain;
B. compounds having an unsaturated chain; and
C. compounds having nuclei in the chain.

Further subdivision is done in accordance with the number and nature of substituents in the macromolecule: hydrocarbons containing alkyl and aryl groups, halogen derivatives, alcohols, amines, acids, etc.

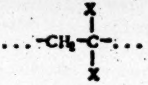
It should be noted that the number of possible compounds of these types is considerably greater than the number already known. This is to be explained on the one hand by the fact that this class of substances became an object for systematic study only comparatively recently, and on the other hand by the fact that the methods known at present for the preparation of carbochain compounds are not suitable for the synthesis of certain groupings. Thus, the polymerization method will yield fairly readily numerous compunds having one and sometimes two substituents of the types:



$$\ldots-CH_2-\underset{X}{\underset{|}{CH}}-\ldots$$

(I)

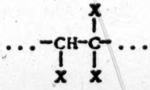
and



$$\ldots-CH_2-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\ldots$$

(II)

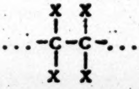
whereas this method, owing to steric hindrance, is in most cases unsuitable for the preparation of compounds containing three or four substituents in the unit [15], i.e. of the types:



$$\ldots-\underset{X}{\underset{|}{CH}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\ldots$$

(III)

or



$$\ldots-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\ldots$$

(IV)

For this reason, the compounds at present known are mainly of Type (I) and, to a less extent, of Type (II); there are very few compounds of Types (III) and (IV).

For the purpose of illustration, the representatives of the group of saturated carbochain compounds known at the present time are given in Table 3.

The second group of carbochain compounds, the unsaturated compounds, are generally prepared by the polymerization of diolefins having conjugated double bonds. The main representatives of the group of unsaturated carbochain compounds are given in Table 4.

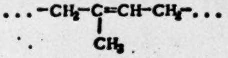
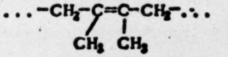
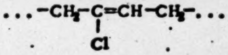
The third group of carbochain compounds are compounds having, as components of their chains, cyclic residues, such as phenyl or cyclohexyl groups having various substituents. These compounds are prepared by the polycondensation of dihalo-substituted hydrocarbons or aldehydes with benzene, its homologs, and its derivatives. The main representatives of this group of compounds are given in Table 5.

B. Heterochain Compounds

We shall give the name of heterochain compounds to all macromolecular compounds that have macromolecular chains consisting not only of carbon atoms or of the atoms of any other single element, but also of atoms of various other elements (oxygen, nitrogen, sulfur, silicon, etc.).

TABLE 4

Unsaturated Carbochain Macromolecular Compounds

Group	Subgroup	Example		
		Name		
		rational	usual	Formula
Unsatd. carbochain hydrocarbons	No substituent	Poly[buten-2-ylene-1,4]	Polybutadiene	$\ldots-CH_2-CH=CH-CH_2-\ldots$
"	Monoalkyl-substd.	Poly[2-methyl(buten-2-ylene-1,4)]	Rubber	 $\ldots-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH-CH_2-\ldots$
"	Dialkylsubstd.	Poly[2,3-dimethyl(buten-2-ylene-1,4)]	Polydimethylbutadiene	 $\ldots-CH_2-\underset{\displaystyle CH_3}{\underset{/}{C}}=\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CH_2-\ldots$
Halosubstd.	Monohalo-substd.	Poly[2-chloro(buten-2-ylene-1,4)]	Polychloroprene	 $\ldots-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{C}}=CH-CH_2-\ldots$

The heterochain compounds comprise a large class of macromolecular compounds, the numerous members of which contain not only various atoms of other elements (hetero atoms) in various combinations with a variable number of carbon atoms, but also a variety of substituents.

This class contains natural substances such as cellulose, proteins, and inulin, and also various synthetic products, such as polyesters, polyamides, polyanhydrides; there are many others, playing a great part in the life of animals and plants and having application on a very large scale in various branches of industry. The principal method of preparing heterochain compounds is by the polycondensation of various bifunctional compounds containing two different groups in their molecules, for example, hydroxy acids, amino acids, etc.

$$xHORCOOH \longrightarrow (-ORCO-)_x + xH_2O.$$

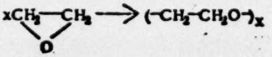
$$xH_2NRCOOH \longrightarrow (-HNRCO-)_x + xH_2O.$$

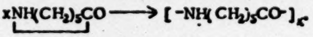
or by the polycondensation of various bifunctional compounds with other bifunctional compounds, for example, dicarboxylic acids with glycols, diamines, etc.

$$xHOROH + xHOOCR'COOR \longrightarrow (-OROOCR'CO-)_x + 2xH_2O;$$

$$xH_2NRH_2 + xHOOCR'COOH \longrightarrow (-HNRNHCOR'CO-)_x + 2xH_2O.$$

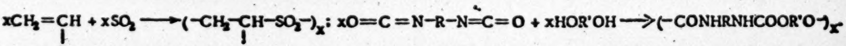
Heterochain macromolecular compounds may be obtained also by the polymerization of heterocyclic compounds such as ethylene oxide, ethyleneimine, caprolactam, caprolactone, etc.





$$x\underbrace{NH(CH_2)_5CO} \longrightarrow [-NH(CH_2)_5CO-]_x.$$

A third method of preparation is the reaction of copolymerization of compounds such as sulfur dioxide with olefins, diazocyanates with glycols or diamines, etc.



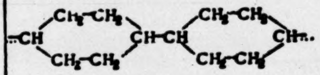
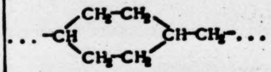
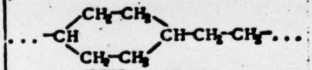
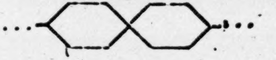
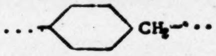
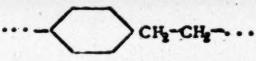
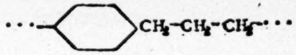
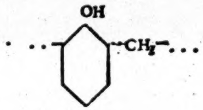
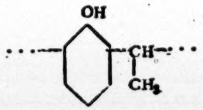
$$xCH_2=\underset{\displaystyle R}{\underset{\vert}{C}}H + xSO_2 \longrightarrow (-CH_2-\underset{\displaystyle R}{\underset{\vert}{C}}H-SO_2-)_x;\ xO=C=N-R-N=C=O + xHOR'OH \longrightarrow (-CONHRNHCOOR'O-)_x.$$

Heterochain macromolecular compounds may be divided, in accordance with the structure of the carbon chain, into the following groups:

A. compounds having a saturated straight chain;
B. compounds having an unsaturated straight chain; and
C. compounds having rings in the chain.

Further subdivision into subgroups is in accordance with the number and nature of the substituents entering into the composition of the chain: compounds having oxygen atoms in the chain, those having nitrogen atoms, sulfur atoms, etc.

Carbochain Macromolecular Compounds Having Chains Containing Aromatic and Hydroaromatic Nuclei

Group	Subgroup	Example		
		Name		Formula
		rational	usual	
Hydrocarbons having hydro-aromatic nuclei	Without methylene groups	Poly(cyclohexamethylene)	–	
•	With one methylene group	Poly(cyclohexamethylenemethyl)	–	
•	With two methylene groups	Poly(cyclohexamethyleneethyl)	–	
Hydrocarbons having aromatic nuclei	Without methylene groups	Poly[phenylene-1,4]	–	
•	With one methylene group	Poly[phenylene-1,4-methyl]	–	
•	With two methylene groups	Poly[phenylene-1,4-ethyl]	–	
•	With three methylene groups	Poly[phenylene-1,4-propyl]	–	
Phenols	With one methylene group	Poly[2-hydroxy(phenylene-1,3-methyl)]	Phenol-formaldehyde resin	
•	With one methylene group, monoalkylsubstd.	Poly[2-hydroxy-1'-methyl(phenylene-1,3-methyl)]	Phenol-acetaldehyde resin	

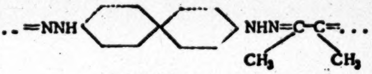
The heterochain compounds constitute a class of substances that is very varied with respect to structure and very large with respect to the number of known representatives. Apart from the large number of natural compounds of this type, a very great number of synthetic heterochain compounds are known at the present time which are distinguished by a number of interesting properties and have found practical application. Although synthetic methods for the preparation of compounds of this class are only in the early stages of development, it is already possible to foresee far-reaching developments in the synthesis of various heterochain compounds in the near future. In order fully to characterize the significance of heterochain compounds, it is necessary to consider the exceptional part that they play in the life of the living cell, where it may be the skeletal material (cellulose), the reverse of nutritive material (starch, inulin), or the basic material substrate of the living cell (protein).

Individual groups of linear heterochain compounds are given in Table 6.

As we have given an exposition only of the principles of chemical classification, we have not touched on such questions as two- and three-dimensional structures of various types, branched chains, etc. There is no doubt, however, that it is possible to include them in this system. It must be added that, since all properties of macromolecular compounds are determined by the structure of the main chain of the macromolecule, the whole complex

TABLE 6

Heterochain Macromolecular Compounds

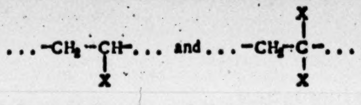
Group	Subgroup	Example		
		Name		Formula
		rational	usual	
Oxygen-containing compounds	Ethers	Poly(hydroxymethylene)	Paraform	$\ldots -OCH_2- \ldots$
″	″	Poly(hydroxyethylene)	Polyethylene oxide, polyethylene glycol	$\ldots -OCH_2CH_2- \ldots$
″	Esters	Poly(hydroxycaproylene)	Polycaprolactone	$\ldots -O(CH_2)_5CO- \ldots$
″	″	Poly(ethylene-adipate)	Polyethylene adipate	$\ldots -O(CH_2)_2OCO(CH_2)_4CC- \ldots$
Nitrogen-containing compounds	Polyamines	Poly(aminoethylene)	Polyethylenimine	$\ldots -NHCH_2CH_2- \ldots$
″	Polyamides	Poly(aminocaproylene)	Polycaprolactam	$\ldots -HN(CH_2)_5CO- \ldots$
″	″	Poly(hexamethyleneadipamide)	Polyhexamethyleneadipamide	$\ldots -NH(CH_2)_6NHCO(CH_2)_4CO- \ldots$
″	Polyhydrazones	Poly(diphenylenediacetyldihydrazone)	Polyhydrazone	
Sulfur-containing compounds	Polysulfides	Poly(tetrathioethylene)	Thiokol	$\ldots -S_4CH_2CH_2- \ldots$

of physical and chemical properties peculiar to a given compound may be expressed as a function of the structure. Chemical properties, in fact, depend on the nature and number of substituents (chlorine, hydroxyl, alkoxyl, carboxyl, carbalkoxyl, alkyl, aryl, etc.) and on the structure of the macromolecular chain itself (presence in the chain of atoms of oxygen, sulfur, nitrogen, etc., and also of various groupings, C=C, rings, etc.). All these atoms and groupings constitute the weak places in the molecule that are most inclined to enter into chemical reactions, and it is these that condition those properties of the substance that are functions of the reactions that occur (stability to acids, alkalis, oxidizing agents, heat, etc.).

These same atoms and groupings, together with the general length and structure of the macromolecule, determine also the whole of that complex of properties that are generally called physical (solubility, stability to frost, thermal stability, plasticity, elasticity, hardness, etc.). They are the source also of forces of interaction between separate chains, i.e. of the magnitude of that effect that used to be called Van der Waals forces, but which is now frequently associated with peculiarities of structure and is explained by the presence of various groups that participate in the formation of various specific chemical bonds.

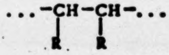
The further, more detailed development of questions in systematics will doubtless be a matter for the future. But even now, it may be remarked that the proposed systematic scheme enables us to form a picture of the whole immense variety of macromolecular compounds, the possibility of whose existence follows from the structural teaching of Butlerov, and to compare them with the few substances that are at present known to us.

It is quite clear that one of the reasons for this is the paucity of methods used at present for the preparation of macromolecular compounds. Thus, polymerization permits us to prepare only those polymers that have one or, occasionally, two substituents in each ethylene residue [16], i.e. of the type:



$$\ldots-CH_2-\underset{X}{CH}-\ldots \text{ and } \ldots-CH_2-\overset{X}{\underset{X}{C}}-\ldots$$

Only rarely does this method permit the preparation of polymers having a substituent on each carbon atom, i.e. of the type:



$$\ldots-\underset{R}{CH}-\underset{R}{CH}-\ldots$$

And it is almost impossible to prepare, by this method, polymers having three or four substituents in the ethylene residue (only two such cases are known, the polymers of trifluorochloro- and tetrafluoroethylene), owing to steric hindrance [16].

Polycondensation appears to be the more universal method, but here also various limitations are encountered: thus in the case of five- and six-membered units, cyclic low-molecular-weight substances are formed more readily than polymers. The equilibrium nature of the process and reactions such as these make it difficult to obtain products of high molecular weight.

These difficulties can evidently be overcome by developing polymerization and polycondensation methods and also by seeking methods for the preparation of macromolecular compounds that are new in principle and are free from the limitations from which the present methods suffer.

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* This reference evidently contains a typographical error. No paper by Korshak appears in the indicated issue.-Pub.

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MACROMOLECULAR COMPOUNDS [1]

COMMUNICATION 53. POLYCONDENSATION OF 1-BROMO-3-CHLOROPROPANE WITH BENZENE

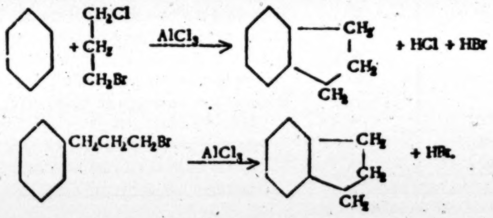
G. S. Kolesnikov and V. V. Korshak

We have previously [2] studied the polycondensation reaction of 1,2-dichloroethane with benzene in presence of aluminum chloride, and have established the main features of this reaction. However, the condensation with benzene of aliphatic halogen compounds having more than two methylene groups between the halogen atoms has received very little study. Thus, the condensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride has been described by Tsukervanik and Yatsimirsky [3], who studied the effect of temperature on the rate of formation of 1,3-diphenylpropane and the possibility of obtaining an alkylhalobenzene. On the basis of their results they concluded that the reaction of 1-bromo-3-chloropropane goes in two stages. First of all, (3-bromopropyl)benzene is formed, and this then reacts with a second molecule of benzene, yielding 1,3-diphenylpropane:

$$C_6H_6 + ClCH_2CH_2CH_2Br \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_2Br + HCl;$$

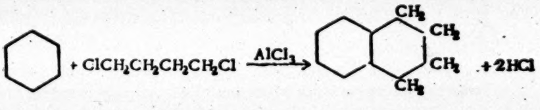
$$C_6H_5CH_2CH_2CH_2Br + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_2C_6H_5 + HBr.$$

It was shown that at 6-12° the first reaction predominates, and (3-bromopropyl)benzene was isolated from the reaction products, but at higher temperatures (80-85°) the rate of the second reaction increases to such an extent that it is not possible to isolate (3-bromopropyl)benzene, and 1,3-diphenylpropane is the main reaction product. The authors pointed out the possibility of the formation of indan by the reaction of 1-bromo-3-chloropropane with benzene in accordance with the following schemes:



but Tsukervanik and Yatsimirsky did not isolate indan: they noted the formation of a resin, which was not investigated further.

The condensation of 1,4-dichlorobutane with benzene in presence of aluminum chloride yields 1,2,3,4-tetrahydronaphthalene as principal reaction product [4]:



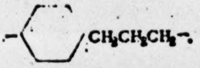
We have undertaken a study of the polycondensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride. Two series of experiments have been carried out. In the first series, which had the object of determining the optimum amount of catalyst, the ratio of benzene to 1-bromo-3-chloropropane was maintained constant, and the amount of aluminum chloride was varied. The duration of the experiment and the temperature were the same in all cases. The molecular weights of the macromolecular reaction products were determined viscosimetrically. The results obtained are given in Table 1.

TABLE 1

Effect of Catalyst Concentration on Yield and Molecular Weight of Polycondensation Product (benzene : 1-bromo-3-chloropropane = 1.3)

Concen. of aluminum chloride (mole-% with respect to benzene)	Macromolecular condensation product	
	Yield (% of 1-bromo-3-chloropropane	Mol. weight
3	10.2	1980
12	18.5	3090
24	32.0	3070
30	50.5	3910
36	55.7	3810

The yield was calculated on 1-bromo-3-chloropropane, it being assumed that one molecule of 1-bromo-3-chloropropane can give one phenylenepropyl residue:



It will be seen from Table 1 that at 30-36 mole-% of aluminum chloride the yield and the molecular weight of the polycondensation products become practically constant. Hence, in the second series of experiments, which had the object of determining the effect of the relative amounts of reacting substances on the yield and molecular weight of the polycondensation products, the concentration of catalyst was maintained constant at 36 mole-% with respect to benzene. The amount of benzene, the temperature, and the duration of the reaction were maintained constant, and the amount of 1-bromo-3-chloropropane was varied. The polycondensation was carried out both in presence of excess of benzene and also in presence of excess of 1-bromo-3-chloropropane. The results obtained are given in Table 2.

TABLE 2

Polycondensation of 1-Bromo-3-chloropropane with Benzene (aluminum chloride concen.: 36 mole-% with respect to benzene)

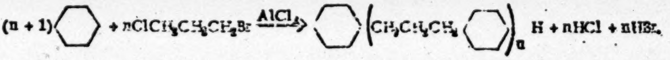
Excess of benzene (mole-%)	Excess of 1-bromo-3-chloropropane (mole-%)	Macromolecular condensation product	
		Yield (%)	Mol. wt.
100	–	39.0*	2800
70	–	39.0*	2460
50	–	47.2*	3940
30	–	55.7*	3810
10	–	45.9*	2650
–	–	56.1*	2070
–	22	66.8**	2310
–	42	61.2**	2080
–	100	84.8**	1950

* With respect to 1-bromo-3-chloropropane

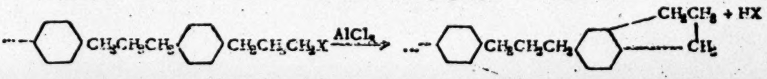
** With respect to benzene

It will be seen from Table 2 that with decrease in the excess of benzene the molecular weight of the polycondensation products rises at first, but then falls, products of maximum molecular weight being obtained with an excess of benzene in the region of 30-50 mole-%. On the basis of the theory of linear polycondensation that one of us has developed [5] it would be expected that products of maximum molecular weight would be formed when the reacting substances are present in equimolecular proportions but this is not so in the present case. This discrepancy may be explained as follows.

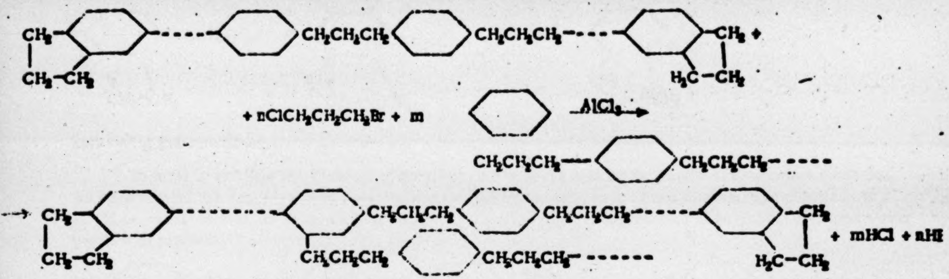
When there is a large excess of benzene, the main reaction is the formation of a linear polycondensation product:



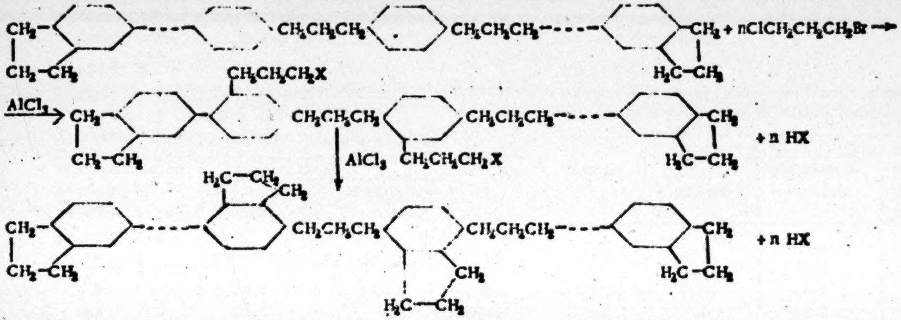
As the excess of benzene is reduced, an ever-increasing effect is shown by a side reaction, proceeding simultaneously with the main reaction, namely, the formation of terminal indanyl groups:



The probability of the formation of such indanyl groups naturally increases as the concentration of 1-bromo-3-chloropropane in the reaction mixture rises. The terminal indanyl groups so formed react with difficulty, or not at all, with 1-bromo-3-chloropropane, for the benzene ring of the indan is already substituted in three positions. As soon as the rate of formation of indanyl terminal groups becomes greater than the rate of formation of linear polycondensation products, the molecular weight of these products will decrease, and this decrease in molecular weight will be the greater, the greater the concentration of 1-bromo-3-chloropropane. When the linear condensation product has an indanyl group at each end (which occurs when there is an excess of 1-bromo-3-chloropropane), it will react with 1-bromo-3-chloropropane and benzene with formation of side chains:



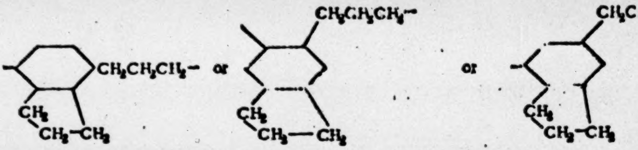
The side chains also may terminate with indanyl groups. The increase in molecular weight due to side-chain formation is not reflected in the molecular weight, as found by the viscosimetric method, which gives an estimate of the maximum size of the molecule. When there is a large excess of 1-bromo-3-chloropropane, indan residues may be formed in the chain of the linear condensation product:



Hence, arresting of chain growth in the polycondensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride is evidently due to the formation of terminal indanyl groups; the low molecular weight of the polycondensation products arises from this cause.

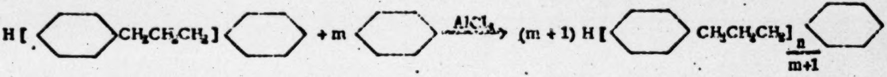
In order to determine the structure of the polycondensation product, we subjected it to destructive oxidation, as we did in the case of polyphenyleneethyl [6]. However, when oxidation was effected by means of chromic acid or by means of acid or alkaline potassium permanganate, it was not found possible to isolate oxidation products in amounts sufficient for the simplest estimations. Only by oxidation with nitric acid (sp. gr. 1.1, warm), and then further oxidation with potassium permanganate in alkaline medium, was it possible to isolate, as principal oxidation product, terephthalic acid, which was identified by its sublimation temperature, its equivalent weight as an acid, and the melting point of its dimethyl ester. In addition to terephthalic acid, an acid was obtained in insignificant amount for which the melting point and equivalent weight were determined; it was not investigated further. On the basis of these determinations this acid is probably p-benzenediacetic acid.

The obtaining of terephthalic and p-benzenediacetic acids as destructive-oxidation products indicates that the polycondensation products of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride are built up essentially from phenylenepropyl units $CH_2CH_2CH_2$—, so that the product may be termed polyphenylenepropyl. In addition to phenylenepropyl units, the main and side chains may contain elementary units of the types



containing indan residues.

In order to confirm the structure of polyphenylenepropyl based on the results of destructive oxidation, we have studied the degradation of polyphenylenepropyl by benzene in presence of aluminum chloride. It would be expected that, as in the case of polyphenyleneethyl [8], the degradation of polyphenyleneethyl would proceed as follows:



with formation of a polyphenylenepropyl of lower molecular weight. The degradation product of lowest molecular weight should be 1,3-diphenylpropane. Our experimental investigations have confirmed these suppositions; the results obtained are shown in Table 3. The low-molecular-weight degradation product that we isolated was 1,3-diphenylpropane, identified by its boiling point, specific gravity, and refractive index.

TABLE 3

Degradation of Polyphenylenepropyl by Benzene in Presence of Aluminum Chloride*

[benzene : polyphenylenepropyl = 8.8 (by weight)]

Relative amounts of aluminum chloride and polyphenylenepropyl (by weight)	Amount obtained		Mol. wt. of polyethylenepropyl
	of 1,3-diphenylpropane (% on wt. of polyphenylenepropyl)	of polyphenylenepropyl (% on original weight)	
0.8	38.0	55.4	2890
1.6	22.4	73.8	2350
2.4	22.0	58.0	2070
3.2	18.8	60.6	2050

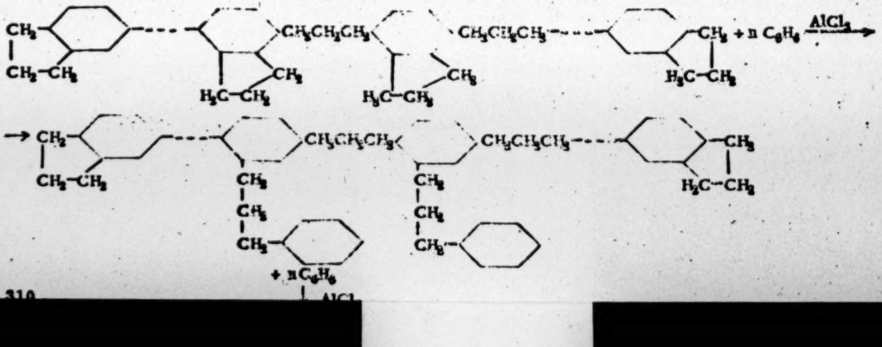
* Mol. wt. of polyphenylenepropyl 3910; duration of reaction, 5 hours.

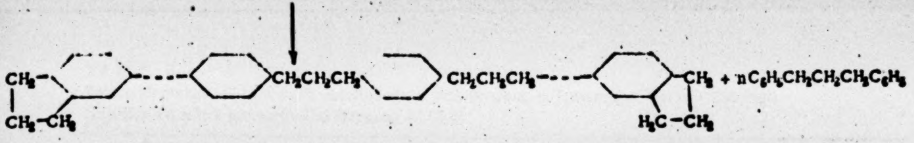
TABLE 4

Polycondensation of 1-Bromo-3-chloropropane with Benzene in Presence of Various Catalysts

Catalyst	Yield (% of theoretical amt.)		Mol. wt. of polyphenylenepropyl
	1,3 diphenylpropane	polyphenylenepropyl	
$AlCl_3$	11.0	47.3	3940
$ZrCl_4$	7.7	52.5	2790
$AlBr_3$	11.8	50.5	2020
$FeCl_3$	12.5	13.9	1350

It will be seen from Table 3 that increase in the amount of aluminum chloride leads to decrease in the molecular weight of the polyphenylenepropyl. This is to be explained by an increase in the number of degradation centers with increase in the concentration of degradation catalyst (aluminum chloride). It was found at the same time that no appreciable change in the molecular weight of the polyphenylenepropyl occurs when the amount of benzene is increased at a constant polyphenylenepropyl : aluminum chloride ratio of 0.625 by weight, but the degradation product has a molecular weight of the same order as that of the original polyphenylenepropyl. As formation of 1,3-diphenylpropane (up to 29% on the weight of polyphenylenepropyl taken) is observed in this case also, absence of change in molecular weight may be explained by degradation taking place mainly in the side chains and by rupture of the saturated rings of the indan residues with formation of side chains, which then react with benzene, giving 1,3-diphenylpropane.





The degradation of 1,2,3,4-tetrahydronaphthalene rings by the action of benzene in presence of aluminum chloride, with formation of 1,4-diphenylbutane, has been previously described by us [7]. The degradation of side chains and of indan rings has no effect on the viscosimetric molecular weight, and consequently no change in this property could be observed by us.

Experiments were carried out also on the polycondensation of 1-bromo-3-chloropropane with benzene in presence not only of aluminum chloride but also of other catalysts: aluminum bromide, anhydrous zirconium chloride, and anhydrous ferric chloride. The results obtained with a benzene : 1-bromo-3-chloropropane ratio of 1.5 and 50.2 mole-% of catalyst on the amount of 1-bromo-3-chloropropane taken are given in Table 4.

It will be seen from Table 4 that the use of zirconium chloride and aluminum bromide leads to equal yields of polyphenylenepropyl, whereas, when ferric chloride is used, the yield is greatly reduced, indicating the low catalytic activity of ferric chloride in the polycondensation of 1-bromo-3-chloropropane with benzene. The molecular weight of the polyphenylenepropyl formed indicates that for this reaction the most active catalyst is aluminum chloride, and the least active is ferric chloride; zirconium chloride and aluminum bromide occupy intermediate places.

EXPERIMENTAL*

The procedure was the same as that used previously [2]. Low-molecular-weight reaction products were distilled off at 5 mm at temperatures of up to 230°. In order to purify it more completely from low-molecular-weight substances, the polyphenylenepropyl was reprecipitated from benzene solution with methanol, a 4% solution of polyphenylenepropyl in benzene being poured dropwise under stirring into six times its volume of methanol. After one day the methanolic solution was poured off, and the precipitated polyphenylenepropyl was dissolved in a small amount of benzene. The benzene solution was transferred to a dish, the benzene was evaporated off, and the polyphenylenepropyl was freed from residual benzene in a vacuum desiccator. The experimental conditions and results obtained are shown in Tables 5-8.

TABLE 5

Effect of Catalyst Concentration on Yield and Molecular Weight of Polycondensation Products

(benzene 38 ml; 1-bromo-3-chloropropane 51.5 g)

Aluminum chloride (g)	Amount obtained		Concen. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. weight
	low-mol. wt. products (g)	polyphenylenepropyl (g)			
1.7	31.8	3.95	2.07	0.0623	1980
6.8	28.9	7.15	2.348	0.1107	3090
13.6	12.5	12.35	3.676	0.1720	3070
17.0	3.65	19.50	0.473	0.0282	3910
20.4	8.7	21.50	1.005	0.0583	3810

TABLE 6

Polycondensation of 1-Bromo-3-chloropropane with Benzene

(benzene 38 ml; aluminum chloride 20.4 g)

1 Bromo-3-chloropropane (g)	Amount obtained		Concen. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. wt.
	low-mol. wt. products (g)	polyphenylenepropyl (g)			
33.5	5.7	9.8	2.449	0.1042	2800
39.35	7.6	11.5	2.535	0.0875	2160
44.35	6.1	15.7	5.969	0.0533	3310
51.5	8.7	21.5	1.005	0.0583	3810
61.0	8.5	21.0	2.056	0.0831	2650
66.7	7.0	28.0	1.560	0.0492	2070
81.6	7.0	33.4	2.574	0.0307	2310
94.6	18.0	30.6	2.531	0.0803	2080
131.0	39.1	42.4	2.100	0.0623	1950

TABLE 7

Degradation of Polyphenylenepropyl by Benzene**

(polyphenylenepropyl 5 g; benzene 50 ml)

1,3-diphenylpropane (g)	Amount obtained		Concen. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. wt.
	low-mol.wt. products(g)	polyphenylenepropyl (g)			
4	1.9	2.77	0.913	0.0402	2890
8	1.12	3.69	2.284	0.0818	2350
12	1.1	2.90	1.713	0.0540	2070
16	0.94	3.03	1.597	0.0500	2050

** Duration of reaction 5 hours; mol. wt. of polyphenylenepropyl 3910.

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*Carried out with the participation of the student K.K. Shinkina.

TABLE 8

Polycondensation of 1-Bromo-3-chloropropane with Benzene in Presence of Various Catalysts (benzene 38 ml; 1-bromo-3-chloropropane 44.35 g)

Catalyst		Amount obtained		Concen. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. weight
Formula	Amount (g)	1,3-diphenylpropane (g)	Polyphenylenepropyl (g)			
$AlCl_3$	20.4	6.06	15.71	0.969	0.0583	3940
$ZrCl_4$	35.7	4.25	17.8	0.916	0.0390	2790
$AlBr_3$	40.8	5.5	16.8	2.697	0.0829	2020
$FeCl_3$	24.8	6.88	4.64	4.177	0.0359	1350

SUMMARY

1. The polycondensation reaction of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride has been studied, and the fundamental features of the reaction have been established.

2. It has been shown that zirconium chloride, aluminum bromide, and ferric chloride are also catalysts for this reaction.

3. An explanation of the results obtained has been given.

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* See Consultants Bureau English translation, page 967.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 56. EFFECT OF STEREOCHEMICAL FACTORS ON THE POLYMERIZABILITY OF HALOGEN-SUBSTITUTED ETHYLENES

V. V. Korshak and N. G. Matveeva

The question of the effect of substituents on the ability of substituted ethylenes to undergo polymerization has attracted the attention of investigators over a long period. These investigators include Butlerov [1], Kondakov [2], Lebedev and Filonenko [3], Shorygin and Shorygina [4, 5], and other workers [6, 7]. As a result of these numerous investigations, a large amount of experimental material has been accumulated which permits an idea to be obtained of the relation existing between the structure of the substituents and the ability of substituted ethylenes to undergo polymerization [8].

One of us has shown that one of the most important factors determining the presence or absence of polymerizability in substituted ethylenes is the number and size of the substituents on the doubly bound carbon atoms [7, 8, 9, 10, 11]. In order to study this factor, we have investigated the polymerizabilities of a large number of unsaturated compounds of various structures and have obtained experimental results that fully confirm the fundamental ideas that were expressed earlier solely on the basis of the material to be found in the literature [7, 9]. In this paper we shall give the results obtained in the investigation of halogen-substituted ethylenes.

The halogen-substituted ethylenes form a class of organic compounds that has been very widely investigated from the point of view of the dependence of their polymerizability on structure. Nevertheless, in the case of a number of halogen-substituted ethylenes the presence or absence of ability to polymerize has not been established in a sufficiently reliable fashion. There are a particularly large number of desiderata of this sort among the iodine- and bromine-substituted ethylenes. We have, therefore, attempted to clear up this matter with respect to tetrachloroethylene, tetrabromoethylene, tetraiodoethylene, 1,1-dibromoethylene, and 1,1-diiodoethylene. There were no definite indications in the literature regarding the tendency of these compounds to polymerize, apart from a reference to the formation of solid substance from 1,1-dibromoethylene in presence of moist air [12]. For the purpose of this work, tetrabromoethylene, tetraiodoethylene, 1,1-dibromoethylene, and 1,1-diiodoethylene were synthesized.

Tetrabromoethylene was prepared from hexabromoethane by the splitting of bromine from the latter during distillation [13]. Tetraiodoethylene was prepared from acetylene and iodine in benzene solution [14]. 1,1-Dibromoethylene was prepared from 1,1,2-tribromoethane by the action of an alcoholic solution of caustic potash. We attempted to prepare 1,1-diiodoethylene from 1,1,1-trichloroethane by the action of aluminum iodide, but the reaction resulted in the formation of a black powder, which, on the basis of the analytical results, may be regarded as a copolymer of the following unsaturated substances: $CH_2{=}CI_2$, $CH_2{=}CICl$, $CH_2{=}CCl_2$, formed by the splitting of hydrogen chloride or iodide from products formed in the reaction of 1,1,1-trichloroethane with aluminum iodide. This result gives us reason to suppose that 1,1-diiodoethylene is a polymerizable compound.

In order to determine their polymerizabilities, tetrachloroethylene, tetrabromoethylene, and tetraiodoethylene were irradiated with ultraviolet radiation (mercury lamp), for 250 hours. Other portions of these compounds were heated, with no addition and in presence of benzoyl peroxide, at 200° for 250 hours. Also, the effect of ionic catalysts was examined, the substances being subjected to the action of aluminum chloride at −60° in chloroform solution. However, none of these three compounds showed any signs of polymerization in these treatments. An attempt to induce polymerization by the use of a high pressure in which tetrachloroethylene was heated at 200° at 5000 atm. was also unsuccessful.

On the other hand, 1,1-dibromoethylene readily polymerized even during standing, and it polymerized still more readily when heated, particularly in presence of benzoyl peroxide. A solid polymer, insoluble in the usual solvents, was formed.

Thus, it was established by these experiments, that tetrachloroethylene, tetrabromoethylene, and tetraiodoethylene do not polymerize, whereas 1,1 dibromoethylene and also, evidently, 1,1-diiodoethylene, polymerize very readily.

DISCUSSION OF RESULTS

We shall now examine how the polymerizability varies in a series of halogen-substituted ethylenes according to the nature and number of the halogen atoms. For the more convenient examination of the position, we give a table showing which of the halogen-substituted ethylenes polyermize and which do not.

TABLE

Polymerizability of Halogen-substituted Ethylenes

Halogen	Internal atomic radius of the halogen (A)	Van der Waals' atomic radius of the halogen (A)	Polymerizing compounds	Nonpolymerizing compounds	Literature reference
I	1.33	2.1	$CH_2{=}CHI$		[15]
			$CH_2{=}CI_2$		—
				$CI_2{=}CI_2$	—
Br	1.14	1.9	$CH_2{=}CHBr$		[15]
			$CH_2{=}CBr_2$		—
				$CBr_2{=}CBr_2$	—
Cl	0.99	1.7	$CH_2{=}CHCl$		[16]
			$CH_2{=}CCl_2$		[17]
				$CCl_2{=}CCl_2$	—
F	0.64	1.4	$CH_2{=}CHF$		[18]
			$CH_2{=}CF_2$		[18]
			$CF_2{=}CF_2$		[19]
F and Cl			$CF_2{=}CFCl$		[20]
			$CF_2{=}CCl_2$		[21]

It is quite clear from the results given in the table that when one or two halogen atoms are present in the substituted ethylene molecule, the resulting substances are able to polymerize. One or two atoms of halogen, therefore, are not able to cause steric hindrance to polymerization. Owing to the fact that the new bond arises between two carbon atoms of which one is bound to halogen atoms and the other has only hydrogen atoms, steric factors do not play an essential part. The picture would be quite different if the polymerizing molecules became united through the carbon atoms that carried two halogen atoms. There can be no doubt that in that case considerable steric hindrance would arise from causes that will be examined in detail below, and this circumstance would make such a polymerization reaction impossible. In illustration of this question, we show some stereochemical models of 1,1-difluoro-, 1,1-dichloro-, 1,1-dibromo-, and 1,1-diiodo-ethylene, in Fig. 1.

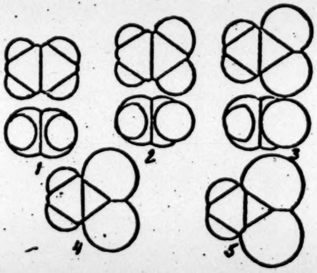

Fig. 1. Stereochemical models of the molecules of: 1) ethylene, 2) 1,1-difluoroethylene, 3) 1,1-dichloroethylene, 4) 1,1-dibromoethylene, 5) 1,1-diiodoethylene.

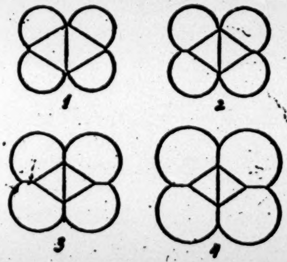

Fig. 2. Stereochemical models of the molecules of: 1) tetrafluoroethylene, 2) tetrachloroethylene, 3) tetrabromoethylene, 4) tetraiodoethylene.

We shall now examine tetrahaloethylenes. The fact that, of these compounds, only tetrafluoroethylene is able to polymerize, whereas tetrachloro-, tetrabromo-, and tetraiodo-ethylenes are not able, must be related to the sizes of the halogen atoms, for in this case there are no other essential differences between these four halogens. Evidently, the small size of the fluorine atom results in there being no steric hindrance to the polymerization of tetrafluoroethylene, and, on the other hand, the large sizes of the atoms of chlorine, bromine, and iodine are responsible for the creation of such great steric hindrance that polymerization becomes impossible. In illustration of this, stereochemical models of the molecules of these halogen derivatives are given in Fig. 2, in which the differences between them are clearly visible.

Thus, it may be concluded that when four identical substituents are present in the ethylene molecule, steric hindrance occurs only when the size of the substituent is equal to or greater than that of the chlorine atom, i.e., 1.7 A or more. This limiting radius may be called the "limiting steric radius". It may be seen that the chlorine atom does lie on the limit by the fact that tetrachloroethylene can, under the influence of elementary fluorine, give the dimer tetrachlorodifluorobutane [22]. It is of interest to note that the Van der Waals atomic radius of the carbon atom is also equal to 1.7 A, and we may conclude that in the case of atoms having a radius greater than that of the carbon atom, steric hindrance will arise owing to the fact that such a substituent does not allow the carbon atoms of the two uniting molecules to effect the necessary contact, which must evidently be complete. We have proposed that this effect should be called the "screening effect".

The final argument for the view that the obstacles to polymerization have a stereochemical character in the case of the tetrahaloethylenes, consists in a comparison of tetrachloroethylene with dichlorodifluoroethylene. Whereas the former does not polymerize, the latter polymerizes very readily [21]. Hence, the replacement of two large chlorine atoms by two small fluorine atoms, eliminates the screening effect and permits polymerization to occur. In illustration of this case, models of chlorotrifluoroethylene, dichlorodifluoroethylene, and 1,1-dichloroethylene are shown in Fig. 3.

EXPERIMENTAL

1,1,2-Tribromoethane

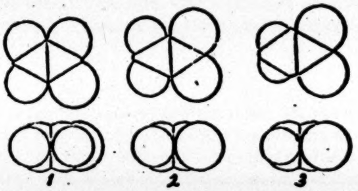

Fig. 3. Stereochemical models of the molecules of: 1) chlorotrifluoroethylene, 2) dichlorodifluoroethylene, 3) 1,1-dichloroethylene.

Methanol (100 ml) and caustic soda (20 g), were introduced into a three-necked flask fitted with reflux condenser, dropping funnel, and thermometer. The reflux condenser was connected to a bubbling tube, which was lowered into a 500-ml cylinder, which was one-third full of a solution of 38 ml (120 g), of bromine in carbon tetrachloride (150 ml). The flask was heated to 55-65° on a water bath, and dropwise addition of dibromoethane from the dropping funnel was commenced (109 g of dibromoethane altogether). The vinyl bromide that was evolved passed through the condenser and was absorbed in the cylinder by the bromine solution. When evolution of vinyl bromide slowed down, the bath temperature was raised to 85°, and heating was continued until evolution of gas ceased.

The solution of tribromoethane in carbon tetrachloride was washed with a sodium thiosulfate solution and then with water. It was dried over calcium chloride, and the carbon tetrachloride was then driven off. The tribromoethane (92.3 g, 48.6%) distilled over at 181-183°.

1,1-Dibromoethylene

Methanol (100 ml), caustic soda (20 g), and hydroquinone (0.5 g), were introduced into a three-necked flask fitted with reflux condenser, dropping funnel, and thermometer. The flask was warmed to 50-60° on a water bath, and 1,1,2-tribromoethane (133 g), was added gradually. When the whole of the tribromoethane had been added, the temperature was raised to 70-80° and maintained at this value for 15 minutes. The reaction mixture was then poured into water, and the oil that separated was washed with water and dried with calcium chloride. Hydroquinone was added to prevent polymerization. The 1,1-dibromoethylene (30.5 g, 33%), distilled over at 87-88°.

Polymerization of 1,1-Dibromoethylene

The polymerization of 1,1-dibromoethylene went readily when it was heated in a sealed tube, without any addition or with the addition of benzoyl peroxide. Appreciable polymer formation occurred when the monomer was stored. Poly-1,1-dibromoethylene (polyvinylidene bromide), is a white powder, insoluble in the usual solvents and decomposing at 140-150°.

Found %: C 12.97; 12.93; H 1.21; 1.18; Br 85.90; 85.85.
$C_2H_2Br_2$. Calculated %: C 12.91 H 1.08; Br 86.00.

1,1,1-Trichloroethane

A 10% solution (25 ml) of aluminum chloride in nitrobenzene was placed in a three-necked flask fitted with reflux condenser, dropping funnel, and tube for passage of gas; 1,1-dichloroethylene (20 ml) was added, and dry hydrogen chloride was passed. Continual addition was made of 1,1-dichloroethylene, the supply being regulated so that practically no hydrogen chloride left the reaction flask [24]. When the whole (150 g) of the 1,1-dichloroethylene had been added, the reaction mixture was allowed to stand for 30 minutes, and was then poured into twice its volume of dilute hydrochloric acid. The oil was separated in a separating funnel, washed with water, and dried with calcium chloride. The 1,1,1-trichloroethane was distilled, the 72-74° fraction (89.6 g, 44.8%) being collected.

Poly-1,1-diiodoethylene (Polyvinylidene Iodide)

Carbon disulfide (100 ml), and iodine (38.5 g) were introduced into a flask fitted with reflux condenser, dropping funnel, and stirrer, and aluminum turnings (3 g) were added in small portions at a time and in such a way as to prevent any considerable rise in temperature. When the whole of the aluminum had dissolved, 1,1,1-trichloroethane (15 g) was added slowly, when the temperature of the reaction mixture rose and it was necessary to cool the flask. When addition of 1,1,1-trichloroethane was complete, stirring was continued for one hour, and the reaction mixture was then poured into dilute hydrochloric acid. The precipitate was filtered off, washed with alcohol, and dried (20.8 g, 61.1%). Polyvinylidene chloride is a black powder, insoluble in the usual solvents; it decomposes when heated.

Hexabromoethane

Hexachloroethane (20 g), and bromine (80 g) were placed in a test tube. Aluminum (4.6 g), first in small pieces and later in large pieces, was stirred into the mixture. At first the reaction was very vigorous: the aluminum floated up to the surface and burst into flame, so that it was necessary to wait until one portion of aluminum had reacted before adding the next. When the whole of the aluminum had reacted, the reaction mixture was poured into dilute hydrochloric acid, and the precipitate that formed was filtered off [23]. Unchanged bromine was removed from the hexabromoethane by washing with dilute alkali and then several times with water. Recrystallization from alcohol yielded hexabromoethane (35.3 g, 76.95%); it decomposes without melting at 200-210°.

Tetrabromoethylene

Hexabromoethane (20 g) was distilled at 180-200° from a Wurtz flask. The mixture of tetrabromoethylene and bromine was collected in a beaker containing caustic potash solution, and the precipitate that formed was filtered off, washed with water, and dried in the air. The dry product was distilled again into a beaker containing alkali, and the precipitate was washed with water, dried, and crystallized from alcohol [13]. The tetrabromoethylene (10.2 g, 74.7%) was formed in glistening plates, m.p. 50-51°.

Tetraiodoethylene

Finely crushed calcium carbide (50 g), and iodine (200 g) were placed in a porcelain beaker, capacity 250-300 ml, and benzene (100 ml) was added under stirring. A stream of nitrogen was passed through a tube that did not reach to the surface of the liquid, and water (120 ml) was added, the temperature being maintained not above 45°. When the whole of the water had been added, stirring was continued for a further one hour. The precipitate was then allowed to settle, and the liquid was carefully poured off. The benzene layer was separated and the benzene was removed, the flask being heated under vacuum on a water bath. The calcium hydroxide settlings were treated several times with dichloroethane at 60-70°, and when the solution was cooled, crystalline tetraiodoethylene separated and was added to the portion obtained from the benzene layer; the mixed sample was recrystallized from dichloroethane [14]. Tetraiodoethylene (69 g, 18%) was obtained in the form of yellow plates, melting with decomposition at 192-193°; it is of very good solubility in carbon disulfide, of good solubility in hot dichloroethane, benzene, and acetic acid, and insoluble in water.

SUMMARY

1. Polymerizability has been investigated in the halogen-substituted ethylene series, tetra- and dihaloethylenes being taken as examples.

2. It has been established that steric hindrance to polymerization in the substituted-ethylene series is determined by the number and sizes of the substituents on the doubly bound carbon atoms.

3. It has been found that the "limiting steric radius" for a substituent, is about 1.4-1.7 A in the case of tetra-substituted ethylenes.

4. It has been shown that in the case of the asymmetrical dihaloethylenes polymerization is possible whatever the halogen may be.

5. The polymerization of 1,1-dibromoethylene has been investigated.

6. It has been shown that tetrabromo-, tetrachloro-, and tetraiodoethylenes are not able to polymerize.

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COMPARATIVE EVALUATION OF THE ACTION OF METAL CHLORIDES IN POLYMERIZATION PROCESSES

COMMUNICATION I. CATALYTIC POLYMERIZATION OF STYRENE IN PRESENCE OF FERRIC CHLORIDE AND OF STANNIC CHLORIDE

M. F. Shostakovsky and V. A. Gladyshevskaya

At the present time it is considered that polymerization processes may proceed by one of two mechanisms: free-radical and ionic. These ideas have been rendered more precise by the investigations of Shostakovsky [1, 2], which have shown that pure polymerization processes do not occur, polymerization being associated with a number of side reactions, of which some result from the interaction of the original monomers with solvents (water, alcohol).

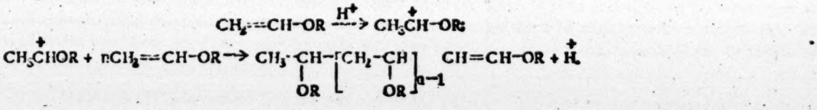
The free-radical mechanism is characteristic for compounds that tend to polymerize in presence of peroxides, oxygen, and a number of substances that are capable of breaking down into free radicals in presence of unsaturated compounds. In general, the free-radical mechanism of polymerization [3, 4], may be represented as follows:

$$\begin{aligned} \text{I.}\quad & RCOOOCOR \rightarrow CO_2 + RCOO + R; \\ & R_1COO + CH_2{=}CHR \rightarrow R_1COOCH_2CHR'; \\ & R + CH_2{=}CHR \rightarrow RCH_2CHR'. \end{aligned}$$

or

$$\begin{aligned} \text{II.}\quad & RCOOOCOR + CH_2{=}CHR \rightarrow [RCOOOCOR + CH_2{=}CHR]; \\ & [RCOOOCOR + CH_2{=}CHR] + CH_2{=}CHR \rightarrow RCH_2CHR' + RCOOCH_2CHR + CO_2 \end{aligned}$$

The catalysts that bring about polymerization by the ionic mechanism are mainly mineral acids and metal chlorides. Polymerization processes of this type [5, 6], are particularly characteristic of vinyl ethers, and may be represented as follows:

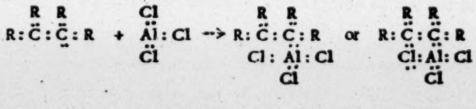


$$CH_2{=}CH{-}OR \xrightarrow{H^+} CH_3\overset{+}{C}H{-}OR;$$

$$CH_3\overset{+}{C}HOR + nCH_2{=}CH{-}OR \rightarrow CH_3{-}\underset{OR}{CH}{-}\Big[CH_2{-}\underset{OR}{CH}\Big]_{n-1} CH{=}CH{-}OR + \overset{+}{H}.$$

The above representations of the mechanisms are not, however, exhaustive: The parts played by the catalysts need to be defined more accurately, and further study of the properties of the original unsaturated compounds is required.

The present investigation has examined the effects of metal chlorides in the reactions of styrene. It has been noted in the literature that styrene may polymerize in presence of metal chlorides, and the delaying and accelerating action of hydrogen chloride has been remarked also. As regards the actual mechanism of the action of metal chlorides: their catalytic action probably results from the intermediate formation of double compounds between these salts and the unsaturated compounds. This mechanism may be represented as follows, aluminum chloride being taken as example: it is supposed that the double bond may be represented by a polarized structure: $>C : C<$, and that the aluminum chloride can accept the electron pair, giving an activated complex, in which, at any given moment, one of the carbon atoms has a covalency of three.



$$R:\overset{R}{\ddot{C}}:\underset{..}{\overset{R}{\ddot{C}}}:R + \overset{Cl}{\underset{\ddot{Cl}}{\ddot{Al}}}:Cl \rightarrow R:\overset{R}{\ddot{C}}:\overset{R}{\ddot{C}}:R \;\; Cl:\underset{\ddot{Cl}}{\ddot{Al}}:Cl \quad \text{or} \quad R:\overset{R}{\ddot{C}}:\overset{R}{\ddot{C}}:R \;\; \ddot{Cl}:\underset{\ddot{Cl}}{\ddot{Al}}:Cl$$

This complex acts as catalyst in the polymerization [7].

The mechanism of the action of stannic chloride, as described by Williams [8] and Gantmakher and Medvedev [9], is based on the same hypothesis. A number of metal chlorides have a chlorinating action [8] (for example, antimony pentachloride), and this complicates the course of the reaction: in polymerization processes, in addition to the polymer, the dichloride $C_8H_8Cl_2$ is formed in an amount that corresponds to half of the amount of added catalyst.

It is doubtful whether it is possible to extend the mechanisms discussed above to all metal chlorides: further detailed and more precise investigation is necessary. Also, generalizations cannot be so readily made about the chemical properties of the chlorides themselves on the basis only of the fact that they can induce polymerization processes, for these processes are extremely sensitive to slight traces of substances having oxidation–reduction properties. It is well known that metal chlorides vary greatly in their oxidation–reduction potentials.

These considerations prompted us to carry out a comparative assessment of the action of metal chlorides on unsaturated compounds in presence and in absence of oxygen. Investigations in this direction showed that ferric chloride acted as a catalyst for the polymerization of styrene only in presence of air. An attempt to effect this process in an atmosphere of nitrogen led to negative results. Stannic chloride, however, brought about polymerization processes both in presence and in absence of oxygen.

Analysis of the polymer obtained in the earlier experiments on the polymerization of styrene under the influence of ferric chloride in an atmosphere of air showed that the product contained a considerable amount of oxygen (16-17%). This suggested to us that the product was a polymeric peroxide, similar to those obtained by Barnes and coworkers [10] by the action of oxygen on styrene. It was found later, however, that when the polymer was submitted to repeated reprecipitation its oxygen content fell (see table). The polymer, after being reprecipitated three times, analyzed as follows: C – 91.15%; H – 8.20% (total 99.35%), and was therefore a practically pure hydrocarbon. The oxygen found in the first analyses did not therefore enter into the constitution of the polymer molecule.

The solvent from which the reprecipitation of the polymer had been carried out was carefully fractionated, and it was found possible to isolate a liquid of b.p. 179° having the characteristic odor of benzaldehyde. The substance was very readily oxidized in the air, giving, as analysis showed, benzoic acid. Thus, in addition to the polymer, benzaldehyde was formed in fairly large amount (8-10 g) in every experiment. The possibility was not excluded that the benzaldehyde was contaminated with benzoic acid, for analysis gave a somewhat exalted oxygen content. The benzaldehyde remained liquid, however, when kept in sealed tubes, no separation of benzoic acid crystals being observed, and the amount of contamination by the acid must have been very slight. Benzoic acid might have been present also in the resin left after removal of solvent and benzaldehyde by distillation, but no acid was isolated from the resin.

Staudinger [11] remarked that the products of the polymerization of styrene in presence of oxygen always contain traces of benzaldehyde. Stobbe [12] also found that when styrene is subjected to the action of light in presence of oxygen, both polymer and benzaldehyde are formed.

As already indicated, an attempt to polymerize styrene in presence of ferric chloride in an atmosphere of nitrogen led to negative results. Also, as it was desired to learn more about the part played by ferric chloride as a catalyst, control experiments were carried out in which styrene was subjected to the action of air in absence of catalyst; conditions of time and temperature were the same as those for the experiments with ferric chloride and access of air. Polymerization did not occur. Fractional distillation of the products obtained in the control experiments and also in the experiments carried out in presence of ferric chloride in a nitrogen atmosphere yielded styrene quantitatively; no benzaldehyde was detected.

It was therefore shown that for polymerization of styrene to occur under our experimental conditions (comparatively short time and without heat) both oxygen and ferric chloride must be present. On the basis of these facts it may be assumed that ferric chloride catalyzes the oxidation of styrene by air, and the peroxide compounds so formed bring about the polymerization of styrene. The presence in our experiments of an appreciable amount of benzaldehyde, formed evidently by the oxidation of styrene, may also play a significant part in the polymerization of styrene in air under the influence of ferric chloride. It is well known that benzaldehyde that has not been specially purified is readily oxidized. It is possible that the oxidation of the aldehyde is a catalytic process occurring only in presence of traces of heavy metals, mainly iron: completely pure benzaldehyde does not oxidize. Rikhe [13] has pointed out that the oxidation of aldehydes proceeds readily in presence of a small amount of an iron salt. It is possible that the ferric chloride present in our experiments catalyzed the oxidation of benzaldehyde. The monoxide formed by the oxidation of the benzaldehyde would rapidly decompose, yielding, in addition to benzoic acid, oxygen in an active form, which would bring about the polymerization of the styrene.

Observations on the variation of the refractive index during the polymerization of styrene in presence of ferric chloride indicated that there was a considerable period of induction. This delay in the onset of the polymerization process may be explained on the hypothesis that at first oxidation processes occurred, and these then brought about the polymerization processes.

As indicated above, polymerization of styrene in presence of stannic chloride evidently proceeds by a completely different mechanism. Polymerization occurred in our experiments both when air was present and when an atmosphere of nitrogen was used. In both cases analysis indicated that the same product had been formed. In all the experiments the onset of polymerization was preceded by a short period of inhibition (10-15 minutes), which may be explained by the presence of hydrogen chloride in the catalyst [8]. In the course of the reprecipitation of the polymers, no side products were detected.

The mechanism of the action of stannic chloride, as we have already noted, has been described in the papers of Williams [8] and Gantmakher and Medvedev [9]. It may be supposed also that stannic chloride, owing to its oxidation-reduction properties, effects polymerization processes both in presence and in absence of oxygen, but this supposition requires further investigation.

TABLE

Composition of Polymer Before and After Purification

Polymer	Analysis		Calc. for
	C(%)	H(%)	$(C_8H_8)_n$
Before reprecipitation	85.60	7.35	% C 92.3 % H 7.7
After the 1st reprecipitation	90.16	7.78	
After the 3rd reprecipitation	91.15	8.20	

EXPERIMENTAL

1. Starting Substances. Freshly distilled styrene was used, distillation being carried out under reduced pressure in an atmosphere of nitrogen. The styrene taken for reaction had the following constants: b.p. 72° at 30 mm; n_D^{20} 1.5460, d_4^{20} 0.9065. The catalysts used were: a 5% solution of $FeCl_3 \cdot 6H_2O$ in absolute butyl alcohol, and $SnCl_4$. The stannic chloride was purified by repeated vacuum distillation.

2. Polymerization of Styrene in an Atmosphere of Air in Presence of Ferric Chloride. The following experiment is typical of the series. It was carried out at room temperature (19-20°) in a three-necked flask fitted with mechanical stirrer, reflux condenser, and thermometer. Styrene (104 g) was poured into the flask, and the catalyst (0.24 g of a 5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) was introduced. Every day at 10 a.m., the refractive index of the mixture was checked, and a further 0.04 g of catalyst was then added. For the first two days of the experiment the refractive index remained unchanged, but, beginning from the third day, it gradually rose. After fourteen days the material, which had become appreciably thicker, was poured into a porcelain dish and left in the air. On the next day the polymer had become solid. The polymer obtained (98 g before reprecipitation) was dissolved in benzene and precipitated from solution with ethanol, after which it was exposed to a vacuum for some time. The reprecipitation was repeated three times, and after each treatment the polymer was analyzed (see the table). The weight of reprecipitated polymer was 86.2 g (82.2%); it had a molecular weight of 5688 * and a viscosity of 1.169 centipoise.

Found %: C 91.15, 91.25; H 8.20, 7.86
$(C_8H_8)_n$. Calculated %: C 92.3; H 7.7

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* In all experiments the viscosity of a solution of 1 g of polymer in 100 ml of benzene was determined at 20° in an Ostwald viscosimeter; the molecular weight was determined cryoscopically in benzene.

The solvent separated from polymer was fractionally distilled, and a liquid of b.p. 70° /20 mm having the characteristic odor of benzaldehyde was isolated. It was very readily oxidized in air, giving a crystalline substance, m.p. 121°; it was confirmed that this was benzoic acid by the following analysis:

Found %: C 68.94, 68.90; H 5.16, 5.09
$C_7H_6O_2$. Calculated %: C 68.8; H 4.91

The benzaldehyde isolated amounted in all to 9.6 g (9.2%).

3. Polymerization of Styrene in an Atmosphere of Nitrogen in Presence of Ferric Chloride. Experiments were carried out in an atmosphere of nitrogen under the conditions described in Section 2. The nitrogen was first passed through bottles filled with pyrogallol for removal of traces of oxygen. In the course of all of the experiments the material remained liquid and its refractive index did not change. After the completion of an experiment, hydroquinone was added to the material in the flask, which was then fractionally distilled, yielding styrene quantitatively; it had the constants: b.p. 45° at 17 mm; n_D^{20} 1.5458, d_4^{20} 0.9070.

4. Polymerization of Styrene in an Atmosphere of Air in Presence of Stannic Chloride. The following experiment is typical of the series. It was carried out at room temperature in the apparatus described for the previous experiments. Styrene (104 g) was poured into the flask and $SnCl_4$ (0.05 g) was added. After 10-12 minutes the temperature of the mixture quickly rose to 130-140° and polymerization set in. The process continued for 40-50 minutes and resulted in the formation of a yellow solid. The polymer obtained (101 g before reprecipitation) was dissolved in benzene and precipitated from solution with ethanol, after which it was subjected to a vacuum for some time. The weight of reprecipitated polymer was 98.8 g (95%), its molecular weight was 1984, and its viscosity, 0.736 centipoise.

Found %: C 91.89, 92.01; H 8.00, 7.90
$(C_8H_8)_n$. Calculated %: C 92.3; H 7.7

Fractionation of the solvents used for reprecipitation of the polymer did not reveal any side products.

5. Polymerization of Styrene in an Atmosphere of Nitrogen in Presence of Stannic Chloride. The experiments were carried out in an atmosphere of nitrogen under the conditions described in Section 4. Both the course of the process and the products obtained were identical with those found when an atmosphere of air was used. We will cite the characteristics of one of the polymers obtained as an example: weight of polymer 100.7 g before reprecipitation, 99.2 g (95.3%) after reprecipitation; molecular weight 2090; viscosity 0.763 centipoise.

Found %: C 91.78, 91.99; H 7.79, 7.74
$(C_8H_8)_n$. Calculated %: C 92.3; H 7.7

Fractionation of the solvents used for reprecipitation of the polymer did not reveal any side products.

6. Control Experiments with Styrene in an Atmosphere of Air without Catalyst. The experimental conditions were the same as those used for the study of the polymerization of styrene in an atmosphere of air in presence of $FeCl_3 \cdot 6H_2O$, with the exception that catalyst was not present. In all the experiments the materials remained liquid and the refractive index did not change. At the end of an experiment hydroquinone was added to the contents of the flask, which were then fractionated, giving a quantitative yield of styrene having the following constants: b.p. 51.5° at 20 mm; n_D^{20} 1.5454; d_4^{20} 0.9063. No side products were found.

SUMMARY

1. The polymerization of styrene in presence of ferric chloride and in presence of stannic chloride has been studied.

2. It has been established that when styrene is polymerized in an atmosphere of air in presence of ferric chloride both polystyrene and benzaldehyde are formed.

3. In an atmosphere of nitrogen and in presence of ferric chloride, styrene does not polymerize.

4. When the process is activated by stannic chloride, the polymer of styrene is formed both in an atmosphere of air and in an atmosphere of nitrogen.

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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

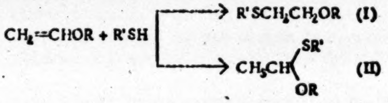
COMMUNICATION 6. REACTIONS OF THIOLS WITH VINYL ETHERS

M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

The addition in accordance with Markovnikov's rule of a number of substances to vinyl ethers evidently has an ionic mechanism: it has been studied in some detail by one of us and coworkers [1]. On the other hand very little is known about the reactions of vinyl ethers that may be interpreted as being of the free-radical type. Thus, there are data about copolymerization reactions of alkyl vinyl ethers with other substances in presence of peroxides [2], and also about the addition of carbon tetrachloride to butyl vinyl ether in presence of benzoyl peroxide [3]. Finally, the partially "abnormal" addition to certain vinyl ethers of hydrogen sulfide and of the alkoxyethyl thiols formed has been the subject of some of our previous communications [4a, 4b, 4c]. The reaction was carried out in presence of small amounts of hydrogen chloride as catalyst in dioxane.

In this connection, it was considered to be of interest to study the products of the reaction of vinyl ethers with thiols, since the particular tendency of the latter to undergo "abnormal" addition of the free-radical type is generally known [5]. This has been carried out in the present investigation, ethyl vinyl and butyl vinyl ethers being taken as examples. As thiols, the following were taken: ethanethiol, 1- and 2-alkoxyethanethiols, and (in one case) thioacetic acid.

The results obtained indicate that the reaction is a very peculiar one, not only the "abnormal" product, which is always obtained when thiols react with olefins [5], being formed. The product is a mixture of a diether of 2-mercaptoethanol (I) (the "abnormal" product) and a monothioacetal (II) (the "normal" product), the former predominating:



$$CH_2{=}CHOR + R'SH \begin{cases} \longrightarrow R'SCH_2CH_2OR \quad (I) \\ \longrightarrow CH_3CH{<}^{SR'}_{OR} \quad (II) \end{cases} \qquad (1)$$

The composition of the mixture depends both on the nature of the ether taken and also on the nature of the thiol (see Table 1). Ethyl vinyl ether reacts with a greater velocity than butyl vinyl ether, and it gives a greater yield of "abnormal" products. Among the thiols, the highest percentage of "abnormal" addition is given by those that are more easily oxidized (1-alkoxyethanethiols, thioacetic acid). The more stable thiols (ethanethiol, 2-alkoxyethanethiols) form up to 40% of "normal" products with butyl vinyl ether, although the reaction is in this case very slow at room temperature and may be brought to completion only by the application of heat.

A completely unexpected effect was shown on this reaction by the substances formed when vinyl ethers or thiols are allowed to stand in the air. These "peroxide" compounds (at least in the case of ethyl vinyl ether and ethanethiol) have no catalytic effect on the abnormal reaction; on the contrary, they retard it. As a result, the composition of the products and the rate of reaction depend greatly on the way in which the starting materials are purified (see Table 4), though in a sense that is the reverse of that required by Kharash's peroxide theory [6]*

We have established also that when freshly distilled vinyl ether and thiol, not containing peroxides, are introduced into an ampoule, which is evacuated under cooling and then sealed, then, whatever the structures of the substances may be, slow formation occurs of the abnormal product only, namely, the diether of

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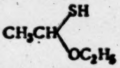
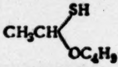
* The only similar fact that we have found in the literature is the observation of Hoog and Eichwald that a mixture of heptane and 1-octene that has been kept in the air for a long period and contains peroxides unites with mercaptoacetic acid more slowly than a freshly prepared mixture does [7]. The authors do not indicate the direction of the addition.

TABLE 1

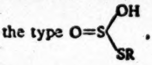
Products Formed by Reaction of Freshly Distilled Vinyl Ethers with Thiols in Presence of Air (Equation 1)

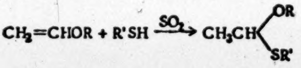
Vinyl ether	Thiol	Composition of reaction products (%)	
		(I)	(II)
$CH_2{=}CHOC_2H_5$	C_2H_5SH	92-97	8-3
$CH_2{=}CHOC_2H_5$	 $\mathrm{CH_3CH}\Big\langle{}^{\mathrm{SH}}_{\mathrm{OC_2H_5}}$	100	–
$CH_2{=}CHOC_4H_9$	C_2H_5SH	60-70	40-30
$CH_2{=}CHOC_4H_9$**	$C_4H_9OCH_2CH_2SH$**	60-65	30-35
$CH_2{=}CHOC_4H_9$	 $\mathrm{CH_3CH}\Big\langle{}^{\mathrm{SH}}_{\mathrm{OC_4H_9}}$	90-91	10-9
$CH_2{=}CHOC_4H_9$	CH_3COSH	100	–

2-mercaptoethanol (Equation 2). When the mixture is heated at 60-70°, a quantitative yield of this product can be readily obtained (see Experimental):

$$CH_2{=}CHOR + R'SH \xrightarrow{O_2} R'SCH_2CH_2OR \quad (2)$$

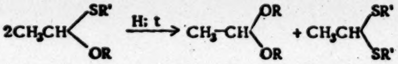
We consider that the reaction is catalyzed by traces of oxygen that remain, under these conditions, in the liquid and on the walls of the ampoule. We have thus obtained also a second unexpected result: the presence of oxygen in large amounts (when the reaction is carried out in air) causes a general acceleration of the reaction, but, at the same time, formation of "normal" addition products.

The noncatalyzed addition of thiols to alkyl vinyl ethers in accord with Markovnikov's rule is, according to our experimental results, extremely slow under all conditions. The cause of this is probably to be found in the fact that the thiol group scarcely forms hydrogen bonds with other substances, while at the same time hydrogen bonds are essential (according to the hypothesis advanced by one of us [1]) for the formation of the complexes that are precursors in an ionic reaction. Introduction of the very slightest amount of a suitable catalyst of an acidic character induces rapid addition reaction of the thiol in accord with Markovnikov's rule. For this purpose we have made use of very small amounts of sulfur dioxide, by the aid of which we have previously brought about the addition of hydrogen sulfide to vinyl ethers [8]. It is possible that sulfur dioxide forms compounds of the type  $\mathrm{O{=}S}\Big\langle{}^{\mathrm{OH}}_{\mathrm{SR}}$, with thiols, and these products act as acidic catalysts in this addition reaction (Equation 3):



$$CH_2{=}CHOR + R'SH \xrightarrow{SO_2} \mathrm{CH_3CH}\Big\langle{}^{\mathrm{OR}}_{\mathrm{SR'}} \quad (3)$$

In the reactions of ethanethiol with ethyl vinyl and butyl vinyl ethers, the yield of the monothioacetal, which under these conditions is the sole product (Equation 3), attains 80-85 % *. Under our conditions there were practically no side products, although we have shown previously [4], taking β-alkoxy-substituted monothioacetals as examples, that these compounds are unstable and tend to undergo a disproportionation reaction:



$$2\mathrm{CH_3CH}\Big\langle{}^{\mathrm{SR'}}_{\mathrm{OR}} \xrightarrow{H;\ t} \mathrm{CH_3{-}CH}\Big\langle{}^{\mathrm{OR}}_{\mathrm{OR}} + \mathrm{CH_3CH}\Big\langle{}^{\mathrm{SR'}}_{\mathrm{SR'}} \quad (4)$$

The catalytic addition of thiols to vinyl ethers in accord with Markovnikov's rule proceeds, therefore, very readily, and does not demand the severe conditions required in the analogous reaction with alkenes [11,12,13].

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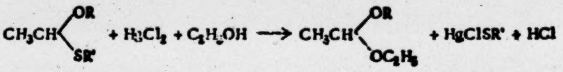
* A number of publications have been published recently on the addition of thiols to vinyl ethers in presence of α-chloro ethers, p-toluenesulfonic acid, and sulfuryl chloride, but the use of these catalysts leads to yields of monothioacetals of not more than 40-45% and to the formation of a large amount of mercaptals as secondary products.

** Unlike the other thiols, for which the reaction was carried out at room temperature, 2-butoxyethanethiols was caused to react at 60-70°.

Thus, in the present investigation we have worked out the conditions for the synthesis from vinyl ethers of two series of compounds that have practically not been described previously, the yields being almost quantitative; these compounds are monothioacetals and diethers of 2-mercaptoethanol.

The identification of these sulfides, and also the analyses of mixtures of isomeric products, was based on the differing behaviors of these two types of compounds toward an alcoholic solution of mercuric chloride. Monothioacetals are quantitatively split by this reagent, as also are other representatives of this series that we have previously prepared from vinyl ethers [4a, 4, 4c] (Equation 5):



$$CH_3CH(OR)(SR') + HgCl_2 + C_2H_5OH \longrightarrow CH_3CH(OR)(OC_2H_5) + HgClSR' + HCl \qquad (5)$$

Diethers of 2-mercaptoethanol give the complex salts usually formed by sulfides under these conditions. The compositions of the mixtures were therefore determined by the previously described method [4a] by titration with a standard alkali solution after treatment of a weighed sample of the material with an excess of an alcoholic solution of mercuric chloride.

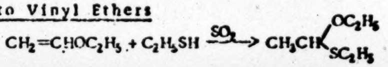
As pointed out above, a number of the regular features that we have discovered in the addition of thiols to vinyl ethers cannot be reconciled with the usual ideas of Kharash's "peroxide" theory. A theoretical treatment of these phenomena will be given on the basis of further supplementary experimental data.

EXPERIMENTAL

In all experiments an excess of the vinyl ether was used: this permitted the end of the reaction to be judged approximately by the disappearance of the thiol odor. All the yields are calculated on the amount of thiol taken for reaction. In most of the experiments, the vinyl ethers were purified by the method employed in the Vinyl Compound Laboratory [14], but, in view of the particular sensitivity of the reactions studied with respect to air oxidation of the vinyl ethers, all the operations of purification and drying were done as quickly as possible. The ether, after being washed with water, was dried for 1-2 days over potassium carbonate, distilled, kept for 1-2 days over sodium, and redistilled just before the experiment. The ether so obtained gave a practically negative test for peroxide with thiocyanate. The thiols were also freshly distilled for use. The method of titrating mixtures of isomeric sulfides has been previously described by us in detail [4a].

I. "Normal" Addition of Thiols to Vinyl Ethers

a) Ethyl vinyl ether and ethanethiol



$$CH_2{=}CHOC_2H_5 + C_2H_5SH \xrightarrow{SO_2} CH_3CH(OC_2H_5)(SC_2H_5)$$

A slow stream of dry sulfur dioxide gas was passed for three minutes through a mixture (previously cooled to −20° in a stream of nitrogen) of ethanethiol (3.9 g) and ethyl vinyl ether (7.2 g) contained in a flask provided with stirrer. The cooling mixture was removed, and the temperature rapidly rose to +30°, the mixture was then again cooled to +15-20°. Stirring was continued at this temperature for a further two hours, and the mixture was then left overnight. The reaction product was vacuum-distilled: the excess ethyl vinyl ether was collected in a cooled trap, and the residue yielded a substance (6.7 g, 81.7%) of b.p. 53-54°/31 mm, n_D^{20} 1.4428.

1-Ethoxy-1-(ethylthio)ethane has b.p. 67.5-68.5° at 50 mm; n_D^{20} 1.4428; d_4^{20} 0.9000; found MR 39.51; calculated MR 39.52.*

Found %:	C 53.64; 53.74;	H 10.57; 10.50;	S 23.54; 23.69
$C_6H_{14}OS$. Calculated %:	C 53.68;	H 10.51;	S 23.89

1-Ethoxy-1-(ethylthio)ethane has a sweetish ethereal odor, which turns rapidly after inhalation into the odor of ethanethiol.

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* The synthesis of this substance from ethyl vinyl ether and ethanethiol in presence of $SOCl_2$ was described by Kipris, Soloway, and Ornfelt [10] when the greater part of the present investigation had been completed. These authors, however, obtained a low yield (40%) of the product, which, moreover, they characterized only by the boiling point (33-35°/5 mm) and analysis for C and H.

The action of an alcoholic solution of mercuric chloride resulted in the quantitative precipitation of ethylthiomercury chloride and the formation of HCl (Equation 4). Titration with standard alkali after the treatment with excess of the alcoholic solution accounted for 96.9% of the theoretical amount of HCl. The substance (0.59 g) with mercuric chloride (1.2 g, as a 20% solution in alcohol) quickly gave a white finely crystalline precipitate, which, after being washed on the filter with dry ether and then dried, weighed 1.40 g (theoretical amount: 1.38 g). This substance did not dissolve in boiling alcohol or ether, and did not melt, but blackened at 350-360°; these properties correspond to those described in the literature [15] for ethylthiomercury chloride.

Found %: S 10.57; 10.50

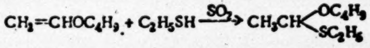
C_2H_5SHgCl. Calculated %: S 10.82

TABLE 2

Conditions of "Abnormal" Addition of Ethanethiol to Ethyl Vinyl Ether

Expt. No.	Amount taken (g)		Duration of reaction (days)	Temperature of reaction	Properties of reaction products			Yield of reaction products (%)
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{20}	
6	6.3	15.0	7	Room	–	–	1.4507	3
8	6.9	16.0	60	Room	76-77	34	1.4507	77.0
15	6.0	15.0	7	Room, apart from 60 hrs at 60°	83.5-84.5	48	1.4508	93.1

b) Butyl vinyl ether and ethanethiol



$$CH_2{=}CHOC_4H_9 + C_2H_5SH \xrightarrow{SO_2} CH_3CH\begin{smallmatrix}OC_4H_9\\SC_2H_5\end{smallmatrix}$$

Ethanethiol (6.8 g) and butyl vinyl ether (15 g) were each distilled in a stream of nitrogen, and were then mixed and cooled by liquid nitrogen in an ampoule having two side tubes. A slow stream of sulfur dioxide was passed through the ampoule for three minutes, and the ampoule, while still being cooled, was connected to an oil pump. After 30 minutes it was sealed off under a residual pressure of 4 mm. The ampoule was set aside at room temperature for 20 hours and then opened. No unchanged ethanethiol was found. The excess of butyl vinyl ether (3.6 g) was distilled off under reduced pressure, and the following fractions were then obtained:

Fraction I, b.p. 36-51° at 4 mm, 1.0 g; n_D^{20} 1.4448

Fraction II, b.p. 49-51° at 3-4 mm, 15.5 g; n_D^{20} 1.4468

A small resinified residue (0.9 g) remained in the flask. Fraction II was practically pure 1-butoxy-1-(ethylthio)ethane obtained in 86.5% yield. Titration with standard alkali after addition of excess of a 20% alcoholic solution of mercuric chloride accounted for 93.5% of the theoretical amount of HCl. After repeated fractionation the substance had b.p. 56-57° at 5 mm; n_D^{20} 1.4461; d_4^{20} 0.8855; found MR 48.76; calculated MR 48.76. A more detailed characterization of this substance is given below, where reference is made to its isolation by fractionation through an efficient column of a mixture of "normal" and "abnormal" products obtained by addition of ethanethiol to butyl vinyl ether in the air.

II. "Abnormal" Addition of Thiols to Vinyl Ethers

a) Ethyl vinyl ether and ethanethiol

$$CH_2{=}CHOC_2H_5 + C_2H_5SH \xrightarrow{O_2} C_2H_5SCH_2CH_2OC_2H_5$$

All the experiments were carried out in an apparatus consisting of three ampoules connected together by a glass four-way piece, one end of which ended in a tap. Two of the ampoules were provided with side tubes having ground stoppers, and the third had a capillary constriction. Freshly distilled ethanethiol and freshly distilled ethyl vinyl ether were respectively introduced into the first two ampoules. The tap was in the closed position, and the two ampoules were cooled by immersion in liquid nitrogen. The apparatus was then connected to a vacuum pump through the tap and was evacuated for 30 minutes to a residual pressure of 3-4 mm. The tap was then closed, the ampoules containing the substances were taken out of the cooling mixture, and their contents were distilled, under the reduced pressure, into the third ampoule (with the constriction), which was immersed for this purpose in liquid nitrogen. When the distillation was complete, the apparatus was again connected to the vacuum pump, and the ampoule was fused off at a residual pressure of 3 mm. When the ampoule was opened, unchanged vinyl ether and thiol were distilled under reduced pressure into a well cooled trap. The residue was distilled at 35-50 mm.

It will be seen from Table 2 that reaction is not complete at room temperature even after two months. When the mixture was heated to 60-65°, a good yield of 1-ethoxy-2-(ethylthio)ethane — the only reaction product — was obtained in seven days, in the course of which heat was applied for a total period of 60 hours.

1-Ethoxy-2-(ethylthio)ethane has b.p. 78-78.5° at 35 mm; n_D^{20} 1.4507; d_4^{20} 0.9126; found MR 39.57; calculated MR 39.52.

Found %: C 53.54; 53.76; H 10.54; 10.55; S 23.95; 24.17
$C_6H_{14}OS$. Calculated %: C 53.68; H 10.51; S 23.89

TABLE 3

Conditions of "Abnormal" Addition of Ethanethiol to Butyl Vinyl Ether

Expt. No.	Amount taken (g)		Duration of reaction (days)	Period of heating at 60° (hr)	Properties of reaction products			Yield of reaction products (%)
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{20}	
5 a)	9.0	19.5	3	12	65-66.5	4.5	1.4521	44.9
8 a)	5.6	15.0	7	35	65-66	5	1.4520	47.9
7 b)	5.2	15.2	6	35	62-63	4	1.4520	96.8
3 a)	6.8	15.0	40	Not heated	86.5	11	1.4520	78.1

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a) Carried out in the three-ampoule apparatus.
b) Carried out in an ampoule having a constriction.

1-Ethoxy-2-(ethylthio)ethane is a colorless liquid of sweetish odor — somewhat more pleasant than that of the isomeric monothioacetal. With mercuric chloride in alcoholic solution it forms a viscous liquid complex compound, the composition of which was not investigated, and in the course of the reaction the medium remains neutral to Methyl Orange.

It is oxidized very vigorously by hydrogen peroxide in acetic acid with formation of the corresponding sulfoxide; when 1-ethoxy-2-(ethylthio)ethane (10 g) was oxidized with a solution of 29.6% H_2O_2 (9 ml) in glacial acetic acid (16 ml), the product was a substance (the sulfoxide; 5.7 g, 50.7%) having b.p. 112.2-113.5° at 6 mm; n_D^{20} 1.4696; d_4^{20} 1.0354; found M (cryoscopically in benzene) 145.5; 147.5; calculated M 150.2; found MR 40.45; calculated MR 40.14.

Found %: C 48.29; 48.09; H 9.45; 9.65; S 21.44; 21.69
$C_6H_{14}O_2S$. Calculated %: C 47.96; H 9.39; S 21.30

b) Butyl vinyl ether and ethanethiol

$CH_2{=}CHOC_4H_9 + C_2H_5SH \xrightarrow{O_2} C_2H_5SCH_2CH_2OC_4H_9$

The reaction between butyl vinyl ether and ethanethiol, under the conditions described above for ethyl vinyl ether, proceeds more slowly and requires a longer period of heating (see Table 3). The reaction is effected somewhat more rapidly by introducing the two reactants not into the above-described apparatus, but into an ampoule having a capillary constriction, which is then cooled, evacuated to a residual pressure of 3-4 mm, and sealed off. Under these conditions, evidently, a somewhat greater amount of oxygen remains dissolved in the reaction mixture. The reaction conditions will be clear from Table 3.

The only reaction product obtained in all of the experiments was 1-butoxy-2-(ethylthio)ethane, b.p. 65-66° at 5 mm; n_D^{20} 1.4520; d_4^{20} 0.8979; found MR 48.77; calculated MR 48.76 (for a more detailed characterization see below, where a description is given of the isolation of this substance by fractionation through a column of the reaction mixture obtained by the action of ethanethiol on butyl vinyl ether in presence of air). In its properties the substance is reminiscent of 1-ethoxy-2-(ethylthio)ethane.

With mercuric chloride, 1-butoxy-2-(ethylthio)ethane gives a liquid complex compound, and the medium remains neutral during the reaction. 1-Butoxy-2-(ethylthio)ethane (21.5 g) was oxidized in glacial acetic acid (25 ml) with 27.6% H_2O_2 (16.5 ml) and gave the corresponding sulfoxide (18.3 g, 72.3%), b.p. 112-112.5° at 15 mm; 117.2-117.4° at 3 mm; n_D^{20} 1.4664, d_4^{20} 0.9955; found MR 49.64; calculated MR 49.38.

Found %: C 53.92; 53.98; H 10.23; 10.26; S 17.81; 17.69
$C_8H_{18}SO_2$. Calculated %: C 53.89; H 10.17; S 17.99

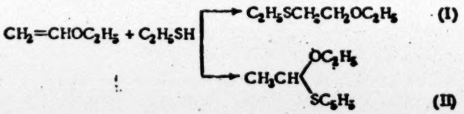
c) Butyl vinyl ether and 2-butoxyethanethiol

$$CH_2{=}CHOC_4H_9 + C_4H_9OCH_2CH_2SH \xrightarrow{O_2} (C_4H_9OCH_2CH_2)_2S$$

Freshly distilled 2-butoxyethanethiol (6 g) of b.p. 47-48° at 5 mm and n_D^{20} 1.4489 [4a] and butyl vinyl ether (15 g) were frozen by liquid nitrogen in an ampoule having a capillary constriction. The ampoule was evacuated to a residual pressure of 5-7 mm and sealed off. Heating at 60-65° was at intervals for a total time of 50 hours in the course of seven days. When the ampoule was opened, no unchanged thiol could be detected. The excess (10 g) of butyl vinyl ether was distilled off, and the residue distilled over completely at 130-131° /4.5 mm (9.4 g, 93.9%; n_D^{23} 1.4560). It did not give a red coloration with Methyl Orange after the addition of mercuric chloride in ethanol. In its properties it corresponded exactly to the previously described bis(2-butoxyethyl) sulfide [4a, 4b].

III. Addition of Thiols to Vinyl Ethers in Presence of Air and of the Oxidation Products of the Starting Materials

a) Ethyl vinyl ether and ethanethiol



$$CH_2{=}CHOC_2H_5 + C_2H_5SH \rightarrow C_2H_5SCH_2CH_2OC_2H_5 \quad (I)$$
$$CH_2{=}CHOC_2H_5 + C_2H_5SH \rightarrow CH_3CH\begin{cases}OC_2H_5\\SC_2H_5\end{cases} \quad (II)$$

A weighed amount of ethyl vinyl ether was mixed with a weighed amount of ethanethiol in a small flask having a ground stopper, and the mixture was allowed to stand at room temperature. Unchanged starting materials were distilled off at 45-50 mm and were retained by a well cooled trap. The residue was distilled from a flask through a fractionating column. The mixture of ethoxy(ethylthio)ethanes was analyzed by titration with alkali after addition of excess of mercuric chloride as a 20% solution in ethanol. The yields, compositions, and constants of the mixtures of sulfides obtained under various conditions with respect to the purification of the starting materials are given in Table 4.

The results given in Table 4 show that freshly purified ethanethiol and ethyl vinyl ether react in presence of air at room temperature appreciably more rapidly than in an evacuated vessel, and they give the "abnormal" product almost exclusively (Experiment 12). Ethyl vinyl ether that has been subjected to the action of the air and contains peroxides unites more slowly with the thiol with formation of a greater amount of "normal" product (Experiments 13, 14 and 16).

Oxidation of the thiol by long storage leads to the same result (Experiment 11). The constants of the mixtures of sulfides (boiling points and refractive indices) correspond, as will be seen from Table 4, to their compositions, as determined by titration. Thus, the products formed by the air-oxidation of vinyl ethers and thiols do not catalyze the addition reaction proceeding contrary to Markovnikov's rule, but retard it.

TABLE 4

Products of the Addition of Ethanethiol to Ethyl Vinyl Ether in Presence of Air

Expt. No.	Amt. taken (g)		Purification of starting materials	Duration of reaction (days)	Properties of reaction products			Yield (%)	Composition (%)	
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{20}		(I)	(II)
12	6.0	15.0	a	7	82-84	47	1.4506	94.6	97.5	2.5
14	6.2	15.0	b	10	82-86	53	1.4502	89.5	90.5	9.5
11	6.2	15.0	c	7	77-84	48	1.4486	78.2	69.5	30.5
16	10.2	25.0	d	6	68-84	53	1.4465	13.3	34.5	65.5
13	5.6	15.0	d	12	75-86	53	1.4495	73.5	78.4	21.6

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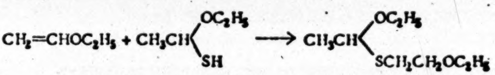
a) The ethyl vinyl ether was washed five times with water and dried with potassium carbonate and sodium. It was distilled twice over sodium before the actual experiment. It gave negative results in the thiocyanate test for presence of peroxides. The ethanethiol was dried over Na_2SO_4 and distilled twice in a stream of nitrogen before the actual experiment (b.p. 35.5-36°).

b) The ethyl vinyl ether, after being washed, was preserved for a month over sodium. It was distilled before the experiment. The thiol was purified as in Expt. 12.

c) The ethyl vinyl ether was purified as in Expt. 12. The ethanethiol was distilled and then preserved in sealed ampoule (in presence of air) for six months. It was not redistilled before the experiment.

d) The ethyl vinyl ether was purified as in Expt. 12 and then left in the air for two weeks. It gave a definite reaction for peroxides. Thiol purified as in Expt. 12 was added to it.

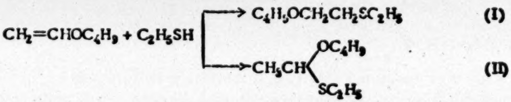
b) Ethyl vinyl ether and 1-ethoxyethanethiol



$$CH_2{=}CHOC_2H_5 + CH_3CH\begin{cases}OC_2H_5\\SH\end{cases} \longrightarrow CH_3CH\begin{cases}OC_2H_5\\SCH_2CH_2OC_2H_5\end{cases}$$

Freshly distilled ethyl vinyl ether (11 g) was added to freshly distilled 1-ethoxyethanethiol (8 g) having b.p. 38-39° at 65 mm and n_D^{20} 1.4378 [3]. After a week the reaction mixture was diluted with an equal amount of ether, washed five times with 5% aqueous KOH and with water, dried, and distilled. The excess of ethyl vinyl ether was distilled off, and further distillation yielded a sulfide (10.8 g. 79.8%) having the properties of 1-ethoxyethyl 2-ethoxyethyl sulfide, which we have described previously [4a]: b.p. 65-68° at 3.5 mm; n_D^{20} 1.4505. Titration with alkali after addition of mercuric chloride indicated a 97.7% content of this sulfide in the fraction described. In the air, 1-ethoxyethanethiol adds to ethyl vinyl ether practically completely in the direction that is contrary to Markovnikov's rule.

c) Butyl vinyl ether and ethanethiol



$$CH_2{=}CHOC_4H_9 + C_2H_5SH \rightarrow \begin{cases} C_4H_9OCH_2CH_2SC_2H_5 \quad (I) \\ CH_3CH\begin{cases}OC_4H_9\\SC_2H_5\end{cases} \quad (II)\end{cases}$$

Butyl vinyl ether unites with ethanethiol in presence of air appreciably more slowly than ethyl vinyl ether, and the reaction cannot be brought to completion without warming (see Table 5). Even freshly distilled materials react with formation of large amounts of the monothioacetal (II) — the addition product corresponding to Markovnikov's rule.

Experiment 2. Freshly distilled ethanethiol (25 g) was mixed in a flask with freshly distilled butyl vinyl ether (60 g), which was purified extremely carefully. The mixture was heated in a sealed ampoule (in presence of air; without evacuation) for 12 hours in a boiling water bath. After two weeks, the excess butyl vinyl ether and

TABLE 5

Reaction between Butyl Vinyl Ether and Ethanethiol in Presence of Air

Expt. No.	Amt. taken (g)		Duration of reaction (days)	Duration of heating		Properties of reaction products		Yield (%)	Composition (%)	
	thiol	ether		hour	temp. (°C)	B.p. (°C)	Pressure (mm Hg)		(I)	(II)
9	6.2	20.0	20	–	Room	65-78	4	12.9	86.4	13.6
1	8.3	27.0	7	8	50	65-70	4	87	37.6	62.4
2	25.0	60.0	14	12	100	57-67	3	89.5	40.5	59.5

a small amount of unchanged ethanethiol were distilled off under reduced pressure. The residue distilled over completely at 57-67°/3 mm, weighed 58.4 g (89.5%), and contained, according to titration, 40.5% of 1-butoxy-1-(ethylthio)ethane. Fractional vacuum distillation of 55 g of this mixture through a column of 20 theoretical plates yielded:

Fraction I (in a cooled trap) 0.6 g; n_D^{20} 1.4439

Fraction II; b.p. 56.1-56.2° at 4 mm, 17.3 g; n_D^{20} 1.4476

Fraction III, b.p. 56.4-67.6° at 4 mm, 5.2 g; n_D^{20} 1.4473

Fraction IV, b.p. 67.6-68.2° at 3.9 mm, 4.5 g; n_D^{20} 1.4519

Fraction V, b.p. 67.8-68.2 at 3.5 mm, 25.1 g; n_D^{20} 1.4521

Fraction II was 1-butoxy-1-(ethylthio ethane* n_D^{20} 1.4476; d_4^{20} 0.8897; found MR 48.79; calculated MR 48.76.

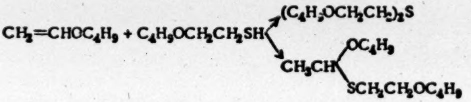
Found %: C 59.37; 59.29; H 11.04; 10.93; S 19.79; 19.70
$C_8H_{18}OS$. Calculated %: C 59.29; H 11.18; S 19.76

By titration with alkali after addition of excess of mercuric chloride, the content of monothioacetal was found to be 96.5%.

Fraction V was 1-butoxy-2-(ethylthio)ethane and did not give an acid reaction in presence of excess of mercuric chloride; n_D^{20} 1.4521; d_4^{20} 0.8931; found MR 48.76; calculated MR 48.76.

Found %: C 59.63; 59.71; H 11.16; 11.20; S 19.82; 20.09
$C_8H_{18}OS$. Calculated %: C 59.20; H 11.18; S 19.76

d) Butyl vinyl ether and 2-butoxyethylethanethiol



$$CH_2{=}CHOC_4H_9 + C_4H_9OCH_2CH_2SH \begin{cases} \rightarrow (C_4H_9OCH_2CH_2)_2S \\ \rightarrow CH_3CH\begin{cases} OC_4H_9 \\ SCH_2CH_2OC_4H_9 \end{cases} \end{cases}$$

2-Butoxyethylethanethiol (0.8 g) [4a] was mixed in a small flask having a ground-in stopper with butyl vinyl ether (2 g). After 20 days, the excess of the ether was distilled off, and further distillation yielded a mixture of sulfides (1.2 g, 85.7%) having b.p. 118-124° at 3 mm; n_D^{20} 1.4552, i.e., the constants of a mixture of 1-butoxyethyl 2-butoxyethyl sulfide with bis(2-butoxyethyl) sulfide [4a]. Analysis by titration after addition of excess of mercuric chloride showed that the mixture contained 34.5% of 1-butoxyethyl 2-butoxyethyl sulfide.

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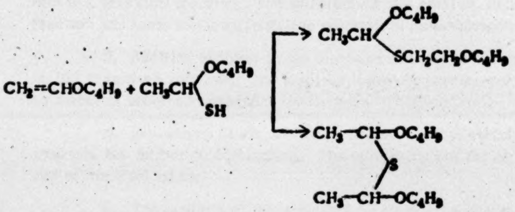
* In the literature the b.p. of this substance is given as 28-30°/2.5 mm [10]. It is probable that the authors were dealing with an impure product.

e) Butyl vinyl ether and 1-butoxyethylethanethiol



Butyl vinyl ether (4 g) was added to 1-butoxyethylethanethiol (2 g) having b.p. 52-53° at 20 mm; n_D^{20} 1.4428 [8], and after a week the products were treated as in the preceding experiment, yielding 2.1 g (60%) of a mixture of sulfides having b.p. 102-106° at 3 mm and n_D^{20} 1.4530, and giving a cream precipitate with mercuric chloride, which is a qualitative reaction for the simultaneous presence of α,β'-dialkoxy- and α,α'-dialkoxy-diethyl sulfides [4a, 4b]. Titration with alkali after addition of excess of mercuric chloride showed that the mixture contained 90.4% of 1-butoxyethyl 2-butoxyethyl sulfide and 9.6% of bis(2-butoxyethyl) sulfide. It was noted that in this experiment an appreciable amount (about 1 g) of resinous products were formed, thus reducing the yield of sulfides.

f) Butyl vinyl ether and thioacetic acid

$$CH_2{=}CHOC_4H_9 + CH_3COSH \longrightarrow CH_3COSCH_2CH_2OC_4H_9$$

Freshly distilled thioacetic acid (b.p. 87-90°; 9.3 g) was added to butyl vinyl ether (30 g) in a small flask having a ground-in stopper. The rise in temperature was so rapid that it was necessary to cool the mixture with ice water. After two days the reaction products were vacuum-fractionated. After removal by distillation of the excess of butyl vinyl ether, the following fractions were obtained:

Fraction I, b.p. 60-92° at 9.5 mm, 1 g

Fraction II, b.p. 92-98° at 9.5 mm, 19.5 g; n_D^{20} 1.4571

the yield of Fraction II being 90.7%.

Evidently, only 2-butoxyethyl thiolacetate was formed, for it was not found possible (by fractionation through a column of 20 theoretical plates) to isolate a fraction corresponding in properties to 1-butoxyethyl thiolacetate, previously synthesized by us from 1-butoxyethanethiol [8]. 1-Butoxyethyl thiolacetate has b.p. 61.7-62.3° at 3 mm; n_D^{20} 1.4560 and d_4^{20} 0.9664 [8]. Fractionation through the column of 23.1 g of the united products from two similar experiments gave:

Fraction I, b.p. 53.5-82.6° at 5.1 mm, 1.0 g; n_D^{20} 1.4420

Fraction II, b.p. 82.6-84.0° at 5.1 mm, 5.0 g; n_D^{20} 1.4600

Fraction III, b.p. 84.0-84.1° at 5.1 mm, 15.1 g; n_D^{20} 1.4605

Thus, the bulk of the substance distils over within a narrow range of temperature. Fraction III was found to have: d_4^{20} 0.9805; found MR 49.28; calculated MR 48.77.

Found %: C 54.43; 54.65; H 9.14; 9.15; S 17.95; 18.00
$C_8H_{16}O_2S$. Calculated %: C 54.51; H 9.15; S 18.19

Thioacetic acid unites vigorously with butyl vinyl ether with formation only of products formed by addition in the direction contrary to Markovnikov's rule.

SUMMARY

1. Methods have been developed for the synthesis from vinyl ethers and thiols of two series of sulfides: monothioacetals (1-alkoxy-1-(alkylthio)ethanes) and diethers of 2-mercaptoethanol (1-alkoxy-2-(alkylthio)ethanes).

2. It has been shown that the noncatalyzed addition of thiols to vinyl ethers in accord with Markovnikov's rule is a very slow reaction. The introduction of a catalyst, such as traces of sulfur dioxide, accelerates this reaction and leads to the quantitative synthesis of monothioacetals.

3. Addition of thiols in the direction contrary to that given by Markovnikov's rule is readily effected in a sealed evacuated ampoule. The reaction is greatly accelerated by rise of temperature, and is evidently catalyzed by traces of dissolved oxygen.

4. In presence of air, addition of thiols to vinyl ethers gives mixtures of "abnormal" and "normal" products, the former predominating. The composition of the mixture depends on the mixture of the vinyl ether and of the thiol taken.

5. The products of the oxidation by air of vinyl ethers and thiols do not accelerate abnormal addition, but, on the contrary, slow it down, which is in conflict with certain consequences of Kharash's peroxide theory.

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* See Consultants Bureau English translation, page 459 ff.

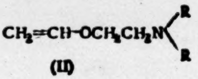
SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 3. NATURE OF THE DOUBLE BOND OF VINYL ETHERS OF ETHANOLAMINES

M. F. Shostakovsky and I. A. Chekulaeva

The present communication relates to an investigation into the synthesis and reactions of vinyl ethers of ethanolamines (2-aminoethanols) of the following structure:

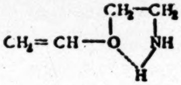
$CH_2{=}CH{-}OCH_2CH_2NH_2$; (I)

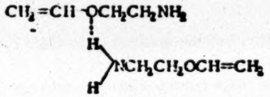


$CH_2{=}CH{-}OCH_2CH_2N\langle^{R}_{R}$ (II)

$(CH_2{=}CH{-}OCH_2CH_2)_2NH$; (III) $(CH_2{=}CH{-}OCH_2CH_2)_3N$. (IV)

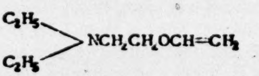
In the previous papers [1,2] it has been noted that the vinyl ether of 2-aminoethanol (monoethanolamine) (I) is less reactive than alkyl vinyl ethers. This is clearly seen from the course of such reactions as hydrolysis and interaction with alcohols. The peculiar behavior of the vinyl ether of 2-aminoethanol is to be explained by the presence in its molecule of a primary amino group in the β-position to the oxygen. The mutual influence of these groups may lead to the formation of intra- and inter-molecular hydrogen bonds according to the scheme:





The presence of a hydrogen bond of this sort hinders the action of the catalyst at the oxygen atom of this vinyl ether and so weakens the activation effect of this compound required by the oxonium mechanism [3].

If this is the explanation of the phenomenon under examination, the double bond in N-substituted vinyl ethers (II), in which there are no mobile hydrogen atoms on the nitrogen, must approximate to a certain extent in character and behavior to the double bond of alkyl vinyl ethers. In order to verify this supposition, a study has been made of the properties of the vinyl ether of 2-(diethylamino)ethanol:



$(C_2H_5)_2NCH_2CH_2OCH{=}CH_2$

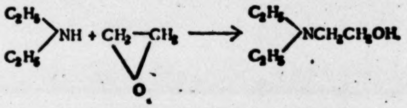
Only the boiling point of this substance is given in the literature [9]. No description has been given of its other properties and of the conditions for its synthesis.

We prepared the vinyl ether of 2-(diethylamino)ethanol by the vinylation of the corresponding alcohol by the reaction developed by Favorsky and Shostakovsky [4,2]

$$ROH + HC{\equiv}CH \xrightarrow{+\,catalyst} CH_2{=}CH{-}OR.$$

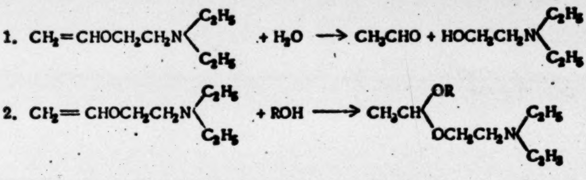
Reaction proceeds in presence of the potassium derivative of 2-(diethylamino)ethanol, giving an 85% yield of the vinyl ether. The use of a solvent (benzene) increases the yield of this vinyl ether to 95-98%. There is practically no catalytic vinylation of 2-(diethylamino)ethanol in presence of caustic potash, no doubt owing to the difficulty with which the potassium derivative of 2-(diethylamino)ethanol is formed under the conditions of vinylation.

The original 2-(diethylamino)ethanol was prepared from ethylene oxide and diethylamine 5,6,7]:



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>NH + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>NCH_2CH_2OH.$$

The chemical reactions of the vinyl ether of 2-(diethylamino)ethanol which were studied, its hydrolysis and addition reaction with alcohols, proceed according to the following equations:



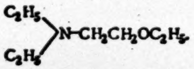
$$1.\ CH_2{=}CHOCH_2CH_2N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + H_2O \longrightarrow CH_3CHO + HOCH_2CH_2N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$$

$$2.\ CH_2{=}CHOCH_2CH_2N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + ROH \longrightarrow CH_3CH\!<\!\begin{matrix}OR\\OCH_2CH_2N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\end{matrix}$$

It was found that the vinyl ether of 2-(dimethylamino)ethanol, unlike that of 2-aminoethanol, is readily and completely hydrolyzed by 2% H_2SO_4 and is able to form acetals.

Thus, taking the hydrolysis and alcohol-addition reactions of the vinyl ether of 2-(diethylamino)ethanol as examples, we have shown that vinyl ethers of 2-aminoethanol in which there are no mobile hydrogen atoms on the nitrogen do indeed approximate in their properties to alkyl vinyl ethers. The presence, however, of two onium centers (O and N) has some effect also in this case. For example, the synthesis of acetals by reaction of the vinyl ether of 2-(diethylamino)ethanol with alcohols required more severe conditions than those required for alkyl vinyl ethers, and gave lower yields (13%) [8].

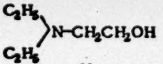
The structure of the vinyl ether of 2-(diethylamino)ethanol was proved not only by its hydrolysis and the synthesis of the acetal, but also by hydrogenation. This reaction was carried out at room temperature over Raney nickel as catalyst, and it led to the formation of the ethyl ether of 2-(diethylamino)ethanol:



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>N{-}CH_2CH_2OC_2H_5.$$

EXPERIMENTAL

Synthesis of 2-(diethylamino)ethanol

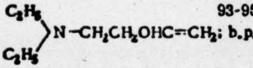
Ethylene oxide (60-70 g) was passed over a period of 4-5 hours into a stirred solution of diethylamine (75 g, b.p. 55-56°; n_D^{20} 1.3870) in water (250 ml). The mixture became warm, and the reaction temperature was maintained at 5-10° by ice-water cooling. The product obtained was salted out with caustic potash, separated from the water, and neutralized by a stream of carbon dioxide. The precipitate that formed was filtered off, and the filtrate was distilled, yielding 2-(diethylamino)ethanol  $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>N{-}CH_2CH_2OH$ (60 g, 50%) as a colorless liquid having a sharp odor. Its constants were: b.p. 159-161°; n_D^{20} 1.4412; d_4^{20} 0.8838; found MR 35.03; calculated $C_6H_{15}ON$ MR 35.37. Data in the literature: b.p. 160° at 741 mm; d^{25} 0.8800; n_D^{25} 1.4389 [6]; b.p. 163° at 760 mm; d_{25}^{25} 0.8601; n_D^{25} 1.4400 [7].

Vinylation of 2-(diethylamino)ethanol

Vinylation was carried out in a stainless-steel rotating autoclave. 2-(Diethylamino)ethanol (b.p. 159-161°; n_D^{20} 1.4412), catalyst (10% on the amount of the original 2-aminoethanol), and a two-fold amount of solvent (benzene) were introduced into the autoclave, and acetylene was passed in up to a pressure of 15 atm; the autoclave was then heated. Caustic potash or the potassium derivative of 2-(diethylamino)ethanol was used as catalyst. The potassium derivative was prepared in a round-bottomed flask with stirrer by addition of potassium to 2-(diethylamino)ethanol, taken in excess, and it was introduced into the autoclave as a solution. The temperature of the vinylation reaction was maintained at 140-150°. Vinylation was continued until the calculated amount of acetylene had been absorbed. Excess of acetylene brought about resinification. The results of the vinylation are given in the table.

TABLE

Expt. No.	Catalyst	Solvent	% Yield of crude vinyl ether	Amt. of resin (% on original 2-aminoethanol)
1	Potassium deriv.	Benzene	95-98	3-5
2	Potassium deriv.	No solvent	83-85	12-15
3	Caustic potash	Benzene	0-0	15-20

The reaction product was a yellowish-red mobile liquid. It was fractionated, at first under reduced pressure, and then at atmospheric pressure. The fraction of b.p. 154-158° at 760 mm was collected, and, with a view to its purification from traces of the original alcohol, it was treated with sodium in the cold and again distilled. The yield of pure product when the vinylation was carried out in benzene in presence of the potassium derivative of the 2-aminoethanol was 93-95%. The analytical results corresponded to the vinyl ether of 2-(diethylamino)ethanol  $(C_2H_5)_2N-CH_2CH_2OHC=CH_2$; b.p. 155-157°; n_D^{20} 1.4328; d_4^{20} 0.8396; found MR 44.31; calculated $C_8H_{17}ON$ MR 44.26. Data in the literature: b.p. 51-55° at 15 mm [9].

Found %: C 67.27; 67.21; H 12.02; 12.24; N 9.90; 10.14

$C_8H_{17}ON$. Calculated %: C 67.10; H 11.96; N 9.78

The vinyl ether of 2-(diethylamino)ethanol is a colorless mobile liquid having a feeble odor; it is soluble in benzene and ether. It was hydrolyzed by 2% H_2SO_4 at room temperature, and the acetaldehyde formed was accounted for quantitatively by the bisulfite method [10]

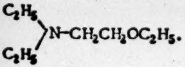
Ester found (%): 100.2, 98.5

Hydrogenation of the Vinyl Ether of 2-(diethylamino)ethanol

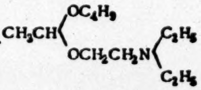
The vinyl ether (b.p. 155-157°; n_D^{20} 1.4328) (13 g) and Raney nickel (0.6 g) were introduced into a 150 ml rotating autoclave, and hydrogen was passed in up to a pressure of 50 atm. Hydrogenation proceeded at room temperature, the theoretical amount of hydrogen being absorbed in 12 hours. The reaction product was filtered off from the catalyst and was distilled at atmospheric pressure. The fraction boiling at 151-155° was collected, and this, after treatment with sodium in the cold, yielded 9.1 g (70%) of a product having the following properties: b.p. 154.5°; n_D^{20} 1.4176; d_4^{20} 0.8145; found MR 44.88; calculated $C_8H_{19}ON$ MR 44.73.

Found %: C 66.27; 65.90; H 13.42, 13.07; N 9.26; 9.50

$C_8H_{19}ON$. Calculated %: C 66.17; H 13.19; N 9.64

The analytical results for this product corresponded to the ethyl ether of 2-(diethylamino)ethanol:  $(C_2H_5)_2N-CH_2CH_2OC_2H_5$. Data in the literature: b.p. 63-64° at 25 mm; n_D^{20} 1.4179 [11].

Synthesis of Acetals from the Vinyl Ether of 2-(Diethylamino)ethanol

1. Acetaldehyde butyl 2-(diethylamino)ethyl acetal  $CH_3CH(OC_4H_9)OCH_2CH_2N(C_2H_5)_2$

a) Synthesis of the acetal by the reaction of the vinyl ether of 2-(diethylamino)ethanol with butanol in presence of concentrated hydrochloric acid. The vinyl ether of 2-(diethylamino)ethanol (b.p. 155-157°; n_D^{20} 1.4328) (13 g, i.e. 0.09 mole) and butanol (b.p. 116-117°; n_D^{20} 1.3990) (6.7 g, i.e. 0.09 mole) were introduced into a round-bottomed flask fitted with stirrer and thermometer. Concentrated hydrochloric acid (3-4 drops) was added under stirring, and the temperature was found to rise from 24° to 26°. The reaction mixture was then heated at 50° for three hours; it darkened considerably. On the next day the reaction product was neutralized with magnesium carbonate, the precipitate was filtered off, and the filtrate (19.1 g) was distilled, at first at atmospheric pressure, and then under reduced pressure. The following fractions were collected:

Fraction I, b.p. 100-125°;	n_D^{18} 1.4087;	3.0 g
Fraction II, b.p. 125-145°;	n_D^{18} 1.4160;	4.8 g
Fraction III, b.p. 145-160°;	n_D^{18} 1.4322;	7.1 g
Fraction IV, b.p. 60-90°/3.5 mm;	n_D^{20} 1.4129;	0.2 g
Fraction V, b.p. 90-100°/3.5 mm;	n_D^{18} 1.4292;	2.7 g
Fraction VI, b.p. 100-110°/3.5 mm;	n_D^{18} 1.4363;	0.4 g
Fraction VII, resin		0.9 g
		19.1 g

Fraction V, after treatment with sodium in the cold, yielded 2.6 g (13.7%) of the required acetal as a colorless liquid having the following constants: b.p. 90-92° at 4.5 mm; n_D^{20} 1.4275; d_4^{20} 0.8670; found MR 64.42; calculated $C_{12}H_{27}O_2N$ MR 64.84.

	Found %:	C 66.46; 66.39;	H 12.50; 12.42;	N 6.45; 6.31
$C_{12}H_{27}O_2N$	Calculated %:	C 66.31;	H 12.53;	N 6.44

The acetal was hydrolyzed with 2% H_2SO_4 at room temperature, and the acetaldehyde formed was determined quantitatively by the bisulfite method:

Acetal found (%): 100.6, 97.2

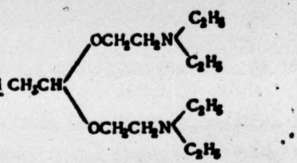
Fractions I, II, and III were mixtures of butanol and the vinyl ether of 2-(diethylamino)ethanol; removal from them of alcohol by means of sodium followed by distillation yielded 9 g of the vinyl ether of 2-(diethylamino)ethanol, b.p. 155-157°; n_D^{20} 1.4328.

b) Synthesis of the acetal from the vinyl ether of 2-(diethylamino)ethanol and butanol by heating in absence of catalyst. The vinyl ether of 2-(diethylamino)ethanol (b.p. 155-157°; n_D^{20} 1.4328) (2.3 g, i.e. 0.016 mole) was heated with butanol (b.p. 116-117°; n_D^{20} 1.3990) (1.2 g, i.e. 0.016 mole) in an ampoule at 230-250° for 15 hours; yellowing occurred. The contents of the ampoule were distilled, at first under reduced pressure, and then at atmospheric pressure. The following fractions were collected:

Fraction I, b.p. 115-117°;	n_D^{20} 1.3995;	0.4 g
Fraction II, b.p. 117-150°;	n_D^{20} 1.4180;	1.2 g
Fraction III, b.p. 150-156°;	n_D^{20} 1.4324;	1.0 g
Fraction IV, b.p. 60-85°/3 mm;	n_D^{20} 1.4130;	0.1 g
Fraction V, b.p. 85-90°/3 mm;	n_D^{20} 1.4280;	0.5 g
Fraction VI, resin		0.3 g
		3.5 g

Redistillation of Fraction V yielded 0.45 g (13%) of the acetal required; it had b.p. 90-92° at 4.5 mm; n_D^{20} 1.4275 (see previous synthesis). Fraction I was butanol. Fractions II and III were treated with sodium and distilled, yielding 1.8 g of the vinyl ether of 2-(diethylamino)ethanol, b.p. 155-157°; n_D^{20} 1.4328.

2. Acetaldehyde bis[2-(diethylamino)ethyl] acetal



$$CH_3CH\begin{cases}OCH_2CH_2N(C_2H_5)_2\\OCH_2CH_2N(C_2H_5)_2\end{cases}$$

The acetal was prepared by heating 15.1 g (0.105 mole) of the vinyl ether of 2-(diethylamino)ethanol (b.p. 155-156°; n_D^{20} 1.4328) with 12.2 g (0.105 mole) of 2-(diethylamino)ethanol (b.p. 159-161°; n_D^{20} 1.4412) in presence of concentrated hydrochloric acid. The reaction temperature was maintained at 100-105° for four hours. The reaction products were treated as in the previous experiment. Fractionation of 24 g of the reaction mixture yielded:

Fraction I. b.p. 155-160°; n_D^{19} 1.4382; 22.4 g

Fraction II. b.p. 115-116° at 4.5 mm; n_D^{19} 1.4410; 1.5 g (6.2%)

Fraction III. resin 0.1 g

24.0 g

Fraction II was a light-yellow liquid, which, according to the analytical results, corresponded to the required acetal: b.p. 115-116° at 4.5 mm; n_D^{20} 1.4410; d_4^{20} 0.8886; found MR 77.83; calculated $C_{14}H_{32}O_2N_2$ MR 78.01.

Found %: C 64.89; 64.73; H 12.80; 12.50; N 11.22

$C_{14}H_{32}O_2N_2$. Calculated %: C 64.57; H 12.40 N 10.76

Fraction I was a mixture of the original 2-(diethylamino)ethanol and its vinyl ether.

SUMMARY

1. Conditions of vinylation of 2-(diethylamino)ethanol have been found that permit the preparation of its vinyl ether in 93-95% yield.

2. The vinyl and ethyl ethers of 2-(diethylamino)ethanol have been prepared and characterized.

3. It has been shown that the vinyl ether of 2-(diethylamino)-ethanol has a greater tendency to hydrolyze and form acetals than the vinyl ether of 2-aminoethanol.

4. The butyl-2-(diethylamino)ethyl acetal and the bis[2-(diethylamino)ethyl] acetal of acetaldehyde have been synthesized.

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 8. CHEMICAL CHANGES IN CELLULOSE PRODUCED BY OXIDATION WITH HYDROGEN PEROXIDE

V. I. Ivanov, E. D. Kaverzneva, and Z. I. Kuznetsova

Hydrogen peroxide is one of the oxidizing agents that have received practical application in the bleaching of cellulosic materials and fibers. Hydrogen peroxide gives the best results when we require a good white in association with high fiber qualities. In our work we have found that a combined hypochlorite-peroxide bleach applied to wood sulfite celluloses that are difficult to bleach yields a high-quality product. It is therefore of both scientific and practical interest to elucidate the chemical processes occurring during the action of peroxide on cellulose.

Hydrogen peroxide is not a specific oxidant, and, under sufficiently severe conditions, oxidation may lead to splitting of carbon–carbon bonds, with complete breakdown of the whole molecule. Ferrous salts catalyze the oxidation reaction. The mechanism of the action of hydrogen peroxide has not yet been fully elucidated. According to the most generally accepted theory, the oxidation of organic substances by hydrogen peroxide in an acid medium is initiated by the reaction between Fe^{++} and H_2O_2, which yields a free hydroxyl radical [1]:

$$Fe^{++} + H_2O_2 = Fe^{+++} + OH^{\cdot} + OH^{-}. \qquad (1)$$

The reaction then develops by a chain mechanism:

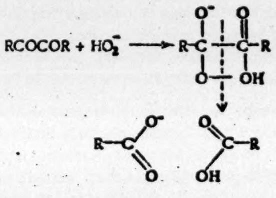
$$CH_3CH_2OH + OH^{\cdot} = CH_3CHOH + H_2O; \qquad (2)$$

$$CH_3\dot{C}HOH + Fe^{+++} = CH_3CHO + Fe^{++} + H^{+}. \qquad (3)$$

According to another variant, oxidation of the organic radical may proceed by reaction with H_2O_2 or $OH^{\cdot}$

$$CH_3\dot{C}HOH + H_2O_2 \longrightarrow CH_3CH(OH)_2 + HO^{\cdot} \longrightarrow CH_3CHO + H_2O + OH.$$

Hydrogen peroxide has its least oxidizing power in neutral solution. Monohydric primary alcohols, for example, do not react under these conditions. In alkaline solution hydrogen peroxide oxidizes compounds of a type that is scarcely affected in acid medium, for example – phenylglyoxylic acid $C_6H_5COCOOH$. The mechanism of the reaction in an alkaline medium has not, as yet, received much investigation. The radical mechanism for this case has been disputed, and the theory that the anion HO_2^- is the active oxidizing agent has been advanced [2]. For the oxidation of a diketone, the following reaction scheme has been proposed:



On the basis of numerous experimental researches on the oxidation of organic compounds with hydrogen peroxide, the following conclusions may be drawn concerning the character of the action of this oxidizing agent on various functional groups. In acid medium in presence of Fe^{++}, hydrogen peroxide oxidizes a primary OH group in monohydric alcohols to an aldehyde or, by further reaction, to a carboxyl group [3]. In 0.2 N H_2SO_4 at 0°, the concentrations of ethanol and H_2O_2 being molar, 41% of the peroxide present was expended in oxidation to acetaldehyde, and the same amount went in the oxidation to acetic acid [4].

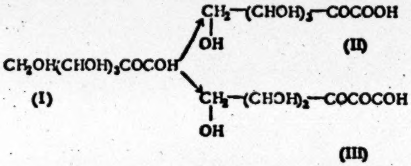
In the oxidation of polyhydric alcohols, reaction occurs first at a primary OH group: glycerol yields glyceraldehyde [5]. The appearance of an aldehyde group, however, reduces the stability of the adjacent secondary OH group, which is then oxidized in its turn. Thus, of the three different functional groups of glyceraldehyde, the least stable to oxidation under these conditions is the secondary alcohol group. The hydroxypyruvaldehyde formed is oxidized then to the acid, and is decarboxylated and decomposed into smaller molecules.

An isolated keto group or an isolated double carbon—carbon linkage is not generally broken down by hydrogen peroxide. When the keto group is conjugated with a C=C or C=O bond, alkaline oxidation rapidly leads to breakdown of the carbon chain [6]. Hence, α-diketones, α-keto aldehydes, and α-keto carboxylic acids are rapidly decomposed in presence of peroxide.

According to Waters [1], in the oxidation of α-glycols, in addition to the main reaction of diketone formation, there is another reaction: splitting of the carbon chain by free OH radicals with formation of aldehydes. Thus, 2,3-butanediol yields 2,3-butanedione and a small amount of acetaldehyde.

In the oxidation of polyfunctional carbohydrate systems and polyhydroxy acids, the course of the reaction is complicated. The first stage of the oxidation of hexoses in acid medium appears to be glucosone; 2-keto acids are generally obtained from hydroxy acids. Here therefore, as in the case of glyceraldehyde, adjacency to a carbonyl or carboxyl group activates a secondary hydroxyl.

It is difficult to establish the further stages of the oxidation of glucosone (I). Kuchlin [7] assumes that oxidation both of the aldehyde and of the secondary hydroxyl group may occur, according to the concentration of the peroxide:



$$CH_2OH(CHOH)_3COCOH \nearrow \underset{OH}{CH_2}-(CHOH)_3-COCOOH \quad \searrow \underset{OH}{CH_2}-(CHOH)_2-COCOCOH$$

(I) (II) (III)

He isolated 2-ketogluconic acid (II), but he advances the compound III as an intermediate product on the basis of the decomposition products found. Thus, predominance of the oxidation of the secondary hydroxyl group or of the aldehyde group depends on the concentration conditions of the reaction.

A certain difference in the direction of the oxidation reaction in presence and in absence of iron may be seen from these experiments of Kuchlin [7] and from work by Jolles [8] on the oxidation of glucose. For oxidation with H_2O_2 in a weakly acid medium in absence of iron, Jolles obtained glucuronic acid: the primary OH group was oxidized to COOH, but the aldehyde group remained unchanged. Kuchlin, working with H_2O_2 in presence of iron, obtained glucosone in the first stage of the reaction, i.e. a secondary OH group was oxidized. However, neither of these authors gives any indication of the amounts of the isolated compounds and of the presence of other oxidation products.

The elementary chain of cellulose contains primary and secondary alcohol groups, glucoside (acetal) bonds, and terminal aldehyde groups. As the oxidation of cellulose by peroxide proceeds in a heterogeneous medium, the factors determining the course of the reaction comprise not only the chemical structure of the molecule, but also the spatial configuration of the macromolecules as a whole and their relative dispositions, which determine the accessibility of particular sections of the chain to the penetration of the oxidizing agent. Mere analogy to the simplest carbohydrates is therefore insufficient for the elucidation of the oxidative breakdown of cellulose under the action of peroxide.

There is a paucity of data in the literature on this question. It is generally considered that hydrogen peroxide reacts with cellulose only in strongly alkaline solution (8% NaOH) [9]. There is then a fall in the viscosity in cuprammonium solution of the treated cellulose. Estimations have been made of the carboxyl

TABLE 1

General Table of the Analyses of Oxycellulose Produced by Hydrogen Peroxide Oxidation*
All results in equivalents per 100 glucose residues

Expt. No.	Oxidation conditions	Reaction of medium	Yield (%)	Coeff. of polymerization	Ash (%)	COOH content			Content of			Notes
						total	uronic	non-uronic	carbonate group	aldehyde group	keto group	
1	5 hrs,40°	pH 4.6	—	244	0.04	0.72	0.53	0.19	1.43	0.61	0.76	Cotton
2	5 hrs,40°	Slightly acid	97.8	220	0.11	1.15	1.01	0.14	2.03	1.39	0.64	Sulfite cellulose
3	5 hrs,40°	"	—	—	—	0.97	0.89	0.08	1.99	—	—	"
4	5 hrs,40°	pH 7	100	1800	0.09	0.13	0.22	—	0.66	—	—	Cotton
5	19 hrs,40° + 119 hrs 25°	Ditto	97.7	680	0.08	0.19	0.46	—	1.19	0.43	0.76	
6	15 hrs, 40° + 81 hrs,18°	"	99.7	390	0.08	0.29	0.85	—	0.98	0.18	0.80	Cellulose oxidized with 18% H_2O_2
7	22 hrs,40° + 98 hrs,18°	"	98.5	265	0.07	0.47	0.72	—	1.29	0.64	0.65	Ditto, 14% H_2O_2
9	48 hrs,18° 2% NaOH	Alkaline	95.6	265	0.09	0.76	0.37	0.39	0.87	0.57	0.30	Cotton
10	5 hrs,40° 8% NaOH	"	85.5	175	0.08	0.81	0.58	0.23	1.05	0.52	0.53	"
11	5 hrs,40° 2% NaOH	"	93.9	244	0.12	0.89	0.29	0.60	1.10	0.32	0.78	"
12	5 hrs,40° 2% NaOH	"	95.7	—	0.08	0.86	0.22	0.64	0.68	0.53	0.15	"
13	111 hrs,40° + 425 hrs,18°; 0.2% NaOh	"	95	162	0.06	1.12	0.64	0.48	0.95	0.61	0.34	"
	Unoxidized cotton			3500	0.19	0.14	0.30		0.50	0.30	0.20	
	Unoxidized sulfite cellulose			800	0.20	0.32	0.76		—	—	—	

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* The H_2O_2 concentration was 5%, except in Experiments 6 and 7; the liquor ratio was 40:1; $FeSO_4$ was added; in Experiments 1-3 an acetate buffer was added, and in Experiments 4-8 a borate buffer of pH 6.8 was added.

groups in oxycelluloses obtained by peroxide oxidation in alkaline medium [10]: after a 5 hr oxidation at 80° with 0.7% H_2O_2, the oxycelluloses contained 0.06-0.08% of COOH groups.

In a recently published investigation of the oxidation of cellulose by hydrogen peroxide in alkaline medium, erythronic acid and other still further degraded products were isolated from the decomposition products [11]. There are also a number of patents and articles in which methods of bleaching celluloses and wood pulps with peroxides are described [12]; questions concerning the chemical changes occurring during the oxidation are not really considered in these publications.

TABLE 2

Distribution of Aldehyde Groups in Oxycelluloses Prepared by H_2O_2 Oxidation

Expt. No.	Conditions of oxidation in 5% H_2O_2	Coefficient of polymerization	Content per 100 glucose residues of			No. in one chain of		
			CHO	Uronic COOH		CHO (total)	CHO at C_6	other CHO
				before NaIO oxidn.	after oxidation			
15	71 hrs, 62°, pH 4.6	250	0.83	0.47	0.64	2.1	0.43	1.67
1	5 hrs, 40°, pH 4.6	244	0.67	0.58	0.63	1.5	0.03	1.47
5	19 hrs, 40° 119 hrs, 25° } pH 7	680	0.43	0.46	0.47	2.9	0.07	2.87
8	52 hrs, 40° 230 hrs, 18° } pH 7	340	0.58	0.47	0.50	1.97	0.10	1.87
9	48 hrs, 18° 2% NaOH	265	0.57	0.37	0.32	1.5	0	1.50
10	5 hrs, 40° 8% NaOH	175	0.52	0.58	0.57	0.9	0	0.9
11	5 hrs, 40°, 2% NaOH	244	0.32	0.29	0.41	0.8	0.29	0.51
14	11 hrs, 40° 60 hrs, 18° } 10% NaOH	162	0.45	0.36	0.58	0.7	0.36	0.34

EXPERIMENTAL

We have studied quantitative changes in the functional groups present in cotton cellulose in conjunction with the changes occurring in the viscosity of its cuprammonium solution, the cellulose being oxidized with hydrogen peroxide under various conditions. The method of investigation was the same as that used in our previous work on the oxidation of cellulose with sodium hypochlorite. The material used in the experiments was cotton cellulose freed from impurities by means of the usual alkaline treatment and by extraction with dichloroethane. After the oxidation (for conditions see Table 1), the oxycelluloses were demineralized in 0.5% acetic acid, washed free from acid, dried at room temperature, and analyzed for their contents of the following functional groups:

1) Total carboxyl groups by the calcium acetate method [13].

2) Uronic carboxyl groups by a micro variant of the method of decarboxylation with 12% HCl [14].

3) Aldehyde groups (iodometrically; borate buffer, pH 9.5; two hours at 25°; titration with 0.01 N $Na_2S_2O_3$ [15].

4) Total carbonyl groups by condensation with hydroxylamine hydrochloride and titration of the free HCl (three hours at 20-25°, pH 5-6; titration with 0.1 N HCl to pH 3.5 (Bromo Phenol Blue)) [16].

5) Nitrogen, after condensation with hydroxylamine, by Kjeldahl. The amount of nitrogen found varied on the average from about 60% to 80% of the amount calculated from the content of carbonyl groups determined by the titration method. The reason for this discrepancy is not altogether clear and we are studying it.

6) Ketone groups from the difference in the carbonyl content (according to nitrogen) and the aldehyde content.

7) The coefficient of polymerization, determined from the cuprammonium viscosity by the formula $p = \frac{\eta}{d \cdot c \cdot K_m}$, where η is the specific viscosity $\frac{\eta_1 - \eta_0}{\eta_0}$, K is taken to be $5 \cdot 10^{-4}$, and c is the concentration of cellulose (g/l).

In most of the experiments the oxidation of the cellulose was carried out in presence of catalyst (0.01-0.1% $FeSO_4$ on the cellulose). Under practical bleaching conditions traces of iron are always present, i.e., the reaction must proceed by the catalytic-oxidation mechanism. We give a general table of the main analytical results (Table 1).

TABLE 3

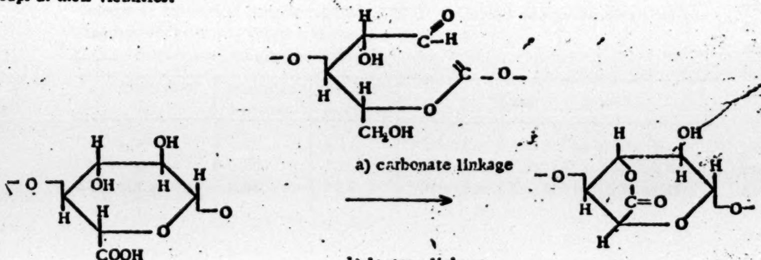
Content of Ketone Groups in the Oxidation of Cellulose (in equivalents per 100 glucose residues)

Expt. No.	Conditions of oxidation	Content of COOH total	Content of CHO	Content of ketone groups	CO/COOH
	Original cotton	0.14	0.40	0.15	1
16	Oxidation in acid medium	0.22	0.83	0.35	1.6
1	Ditto	0.72	0.67	0.76	1.0
2	"	1.15	1.13	0.90	0.8
5	Oxidation in neutral medium	0.19	0.43	0.76	4.0
6		0.29	0.18	0.80	2.8
7		0.47	0.64	0.65	1.4
8		0.52	0.58	0.82	1.6
9	Oxidation in alkaline medium	0.76	0.57	0.30	0.34
10	Ditto	0.81	0.52	0.53	0.65
12	"	0.86	0.53	0.15	0.17
13	"	1.13	0.61	0.34	0.35
14	"	1.19	0.45	0.10	0.08

It may be noted as a general characteristic of peroxide-oxidized celluloses that even under very severe oxidation conditions (5% H_2O_2, in 10% NaOH at 40° for more than 10 hours, or at 90° for 2 hours) the number of oxidized groups remains very low. The maximum carboxyl content in our experiments was 0.34%, or 1.19 equivalents per 100 glucose residues. Oxycelluloses can be obtained by oxidation with an alkaline solution of hypochlorite which have a 1% COOH content, i.e. more than 4 equivalents per 100 glucose residues.

When the total content of COOH groups was determined by the calcium acetate method and the uronic carboxyls were separately estimated by decarboxylation with 12% HCl, the same phenomenon was found as was found also by us for hypochlorite oxidation: for oxidation in a neutral medium, the content of uronic carboxyl groups was higher than the total COOH content of the preparation. There was a difference from the behavior found for hypochlorite oxidation in that whereas the discrepancy extended to acid and neutral oxidation in the case of hypochlorite, it occurred in the present case only for solutions in the neutral region. In an acid medium, there was already a certain preponderance of total COOH content over uronic COOH content.

The causes of this phenomenon were studied by us for oxycelluloses prepared by hypochlorite oxidation [17], and it may be supposed that the same causes account for the increased uronic COOH contents in peroxide oxidation. These causes are: a) the presence of carbonate groups in the constitution of the oxycelluloses oxidized in acid and neutral media, and b) the presence of lactone (ester?) linkages between the uronic carboxyls and hydroxyl groups in their vicinities:



a) carbonate linkage

b) lactone linkage

Both of these linkages constitute blocked acid groups and do not interact with calcium acetate. During heating with 12% HCl both of them give rise to CO_2, giving an exalted value for the free uronic COOH.

As will be seen from the analyses given in Table 1, all the oxycellulose preparations contained aldehyde groups. It follows from the fact that the uronic carboxyl content showed a tendency to rise when supplementary oxidation of aldehyde groups with hypoiodite was effected (Table 2) that a part of the aldehyde groups are to be found at the 6 positions of the glucose residues. Most of the aldehyde groups are converted by oxidation into nonuronic carboxyls. It is possible on the basis of the coefficient of polymerization, with the usual proviso concerning the approximate nature of this method, to calculate the number of aldehyde groups in the average chain of the oxycellulose macromolecule. When the 6-aldehydes are taken into consideration, there remain more aldehyde groups than can on the average be found placed at the ends of chains (except in alkaline oxidation), and it must therefore be supposed that there are also present aldehyde groups formed by oxidation with rupture of the pyran ring, and this we have confirmed by experiments on methyl glucoside.

The figures given in Table 2 have, however, no absolute significance, since oxidation with sodium hypoiodite leads to a loss of carboxyl groups owing to a certain amount of dissolution of the low-molecular-weight fractions of the preparations.

When hydrogen peroxide acts upon cellulose, ketone groups are formed.* They arise at the very beginning of the oxidation: the content of these then rises slightly in acid and neutral media, and undergoes little change in alkaline media.

TABLE 4

Effect of pH on the Rate of Oxidation of Cellulose by H_2O_2

pH during oxidation	Atoms of oxygen bound per 100 glucose residues	Degree of polymerization	Yield of oxycellulose %	Content (per 100 glucose residues)	
				COOH group	CHO + CO group
4.6	3.23	244	–	0.72	1.43
7.0	1.09	1800	100	0.13	0.66
12	3.15	244	93.9	0.89	1.10

Experimental conditions: 5% H_2O_2; liquor ratio 40:1; $FeSO_4$ and buffer added; 5 hrs at 42°.

TABLE 5

Effect of Prolonged Oxidation on the Content of Functional Groups in Oxycellulose (in equivalents per 100 glucose residues)

Conditions of oxidation	Content of				Degree of polymerization
	COOH total	COOH uronic	aldehyde group	ketone group	
Neutral medium, 40°					
5 hrs.	0.13	0.22	–	–	1800
19 hrs.	0.19	0.46	0.43	0.76	680
51 hrs.	0.52	0.47	0.58	0.82	340
Strongly alkaline medium, 40°					
5 hrs.	0.81	0.58	0.53	0.53	175
11 hrs.	1.19	0.35	0.45	0.10	162

TABLE 6

Content of Individual Functional Groups in Oxycelluloses and in the Alkali-soluble Fractions that Go into Solution during the Oxidation (in equivalents per 100 glucose residues)

Content of	Insoluble fraction	Soluble fraction	Notes
COOH, total	0.19	4.14	Oxidation 5 hrs, 40° in 8% NaOH
COOH, uronic	0.58	1.8	Oxidation 11 hrs, 40° in 10% NaOH
Aldehyde group	0.48	27.9	Oxidation 2 hrs, 90° in 0.5% NaOH

It will be seen from Table 3 that in cellulose oxidized in neutral medium ketone groups predominate over carboxyls; there are relatively fewer of them in acid medium, and in alkaline medium they disappear particularly rapidly. At the same time, the number of nonuronic carboxyls increases most rapidly for oxidation in alkaline medium. The positive qualitative reaction for the endiol grouping with a phosphoarsenotungstic reagent gives reason to suppose that a part of the ketone groups present belong to hydroxy ketone groupings that are able to isomerize into endiol groupings in a strongly alkaline medium.

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* In addition to the carbonyl groups, the lactone groups present in the oxycelluloses may react with hydroxylamine. The figures for ketone groups may therefore be somewhat too high.

The rate of the oxidation of cellulose by hydrogen peroxide depends on the pH of the medium. This is shown in Tables 4 and 5. Oxidation proceeds vigorously in strongly alkaline and weakly acid media, and only very slowly in neutral media.

As oxidation is intensified, the most oxidized units of the chains break down and go into solution. This will be seen by comparing the content of functional groups in the water-insoluble oxycellulose with that in its soluble fraction, which separates when its solution is carefully acidified.

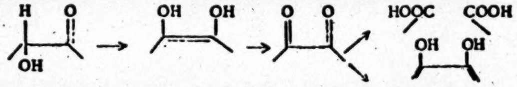
The high content of functional groups of all types in the soluble fractions of the oxycelluloses, as compared with the insoluble part is characteristic. For this reason the chemical composition of celluloses obtained after oxidation is often a poor guide to the extent of the oxidative reactions that have occurred.

Addition of catalyst greatly increases the oxidation process. It will be seen from Table 7 that in the last experiment, in which $FeSO_4$ was added, oxidation went appreciably further than in the first two experiments, in spite of the shorter duration of the experiment and the lower temperature.

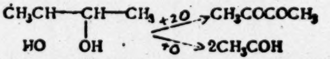
In alkaline medium, the catalyst particularly accelerates the oxidation of secondary OH groups with rupture of the pyran ring and formation of nonuronic carboxyls. This conclusion is in full accord with the results of our investigations on the oxidation of methyl glucoside.

Thus, when cellulose is oxidized with H_2O_2, the same functional groups are oxidized as in the case of the simplest sugars. In the first place, the 6-primary alcohol groups are oxidized to aldehyde groups, and the 2- and 3-secondary OH groups are oxidized to ketone groups. Theoretical considerations indicate that the 2- and 3-hydroxyls are not equivalent, and the 2-hydroxyl should oxidize more readily. This conclusion is in accord with the experimental results obtained for the oxidation of glucose [3]. The formation of ketone groups indicates that in the first stages oxidation of the secondary hydroxyls proceeds without rupture of the pyran ring.

On the basis of considerations given previously [17], it is most probable that the further oxidative breakdown of the pyran ring in strongly alkaline medium (pH > 11) passes through the stages of endiol and diketone:



However, as pointed out above, there are certain indications that when cellulose and also methyl glucoside is oxidized with hydrogen peroxide aldehyde groups are formed at the 2- and 3-positions of the glucose residues. It is therefore probable that breakdown of the pyran ring through the ketone stage is accompanied by a certain amount of oxidative rupture of the ring with formation of two aldehyde groups, as in the reaction established for glycols:



$$\underset{HO}{CH_3CH}-\underset{OH}{CH}-CH_3 \begin{matrix} \xrightarrow{+2O} CH_3COCOCH_3 \\ \xrightarrow{+O} 2CH_3COH \end{matrix}$$

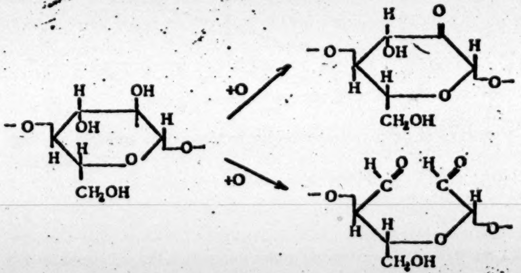


TABLE 7

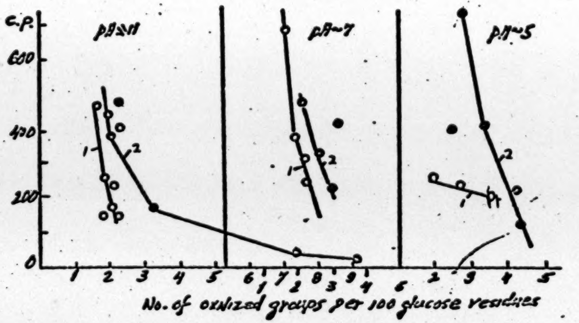
Effect of Catalyst ($FeSO_4$) on the Oxidation of Cellulose with H_2O_2 in Alkaline Medium (pH > 11)

Experimental conditions	COOH group content per 100 glucose res			Coefficient of polymerization	Yield (%)
	total	uronic	nonuronic		
2.5% H_2O_2, 60°, 10 hrs, without $FeSO_4$	0.18	0.29		408	–
5% H_2O_2, 60°, 30 hrs, without $FeSO_4$	0.29	0.25	0.04	236	97
5% H_2O_2, 40°, 5 hrs with addition of $FeSO_4$	0.89	0.29	0.60	244	93.8

TABLE 8

The Ratio CHO/COOH in Oxycelluloses Formed by Oxidation with NaClO and H_2O_2

Prep. No.	Oxidation conditions	CHO/CCOH	Prep. No.	Oxidation conditions	CHO/COOH
	Oxidation with H_2O_2			Oxidation with NaClO	
1	In acid medium	0.93	4	In acid medium	1.23
2	" " "	1.20	1	" " "	1.40
9	In alkaline medium	0.75	7	" " "	1.39
10	" " "	0.64	1a	" " "	1.20
11	" " "	0.36	6	In alkaline medium	0.42
12	" " "	0.60	3	" " "	0.24
13	" " "	0.54	9	" " "	0.12
14	" " "	0.38	"b"	" " "	0.16
16	" " "	0.70	3a	" " "	0.15



Relation between coefficient of polymerization (c.p.) and extent of oxidation:
1) Oxidation with H_2O_2; 2) oxidation with NaClO.

We established that such a course of reaction occurs to an insignificant extent when methyl glucoside is oxidized in cuprammonium solution [19]. The aldehyde and ketone groups formed must oxidize further into carboxyl groups: uronic in the 6-position, nonuronic in the 2- and 3-positions and at the ends of chains in the 1-position.

In the variety of the simultaneously occurring chemical reactions the oxidative breakdown of cellulose under the action of hydrogen peroxide is reminiscent of the breakdown of cellulose when oxidized with hypochlorite. The chemical properties of the oxycelluloses obtained depend in the first place on the pH during oxidation; the nature of the oxidizing agent – H_2O_2 or NaOCl – affects essentially only the quantitative characterization of the properties of the oxycelluloses formed. But in certain respects a qualitative difference is to be observed also. For example, in oxycelluloses obtained by oxidation in an acid medium with hypochlorite, only a negligible amount of nonuronic carboxyls may be formed; none, in fact, can be detected by analysis. In the case of peroxide oxidation in an acid medium, analysis indicates a definite content of nonuronic carboxyls; here, therefore, from the very beginning of the oxidation, we have rupture of the pyran ring, a process which we do not find in the early stages of hypochlorite oxidation.

A second difference lies in the aldehyde content. Oxycelluloses obtained by oxidation with sodium hypochlorite in an acid medium contain a considerable number of aldehyde groups, but in the case of alkaline oxidation the number of aldehyde groups formed is negligible (except when very severe oxidation accompanied by much chain breakdown occurs). No such marked variation in the number of aldehyde groups according to the reaction of the medium is to be observed for hydrogen peroxide oxidation. In order to demonstrate this point, we may compare the ratios of aldehyde to carboxyl groups in the two series of oxycelluloses.

It will be seen from Table 8 that the values of the ratio CHO/COOH for hypochlorite oxidation are widely different for acid and alkaline treatments (the mean values are 1.30 and 0.23 respectively), and that this difference is much less for peroxide oxidation (mean values of 1.06 and 0.73). There is some justification for associating this fact with indications, derived from analyses of the oxycelluloses, of the presence of aldehyde groups formed by the rupture of the 2,3-C–C link.

In this connection, the following peculiarity should be mentioned: if hypochlorite and peroxide oxycellulose preparations having about the same degree of polymerization are compared with one another, it is found that the hypochlorite oxycelluloses contain more oxidized functional groups (the sum of carboxyl and carbonyl groups) (see figure).

From this it may be concluded that the breakdown of the cellulose macromolecule is brought about more readily by the action of peroxide than by the action of hypochlorite. This relation is observed in alkaline, neutral, and acid media. A possible cause of this phenomenon may be the higher temperature employed in the peroxide oxidation (42°, against 20-25° for hypochlorite), leading to a more vigorous attack on the glucoside linkages that have become unstable owing to the proximity of oxidized functional groups. It is more probable, however, that this difference in behavior is caused by this very difference in the content of and character of the aldehyde groups in oxycelluloses produced by the two oxidation processes, and that the temperature factor only intensifies this difference.

It follows, therefore, from a comparison of analytical results that peroxide oxidation of cellulose differs from hypochlorite oxidation with respect to one particular oxidative reaction—the breakdown of a glycol grouping into two aldehyde groupings—which is more in evidence in the first case. This conclusion is based on the greater relative content of aldehyde groups after peroxide oxidation, on the formation of nonuronic carboxyls not only in alkaline, but also in acid media, on the impossibility of finding places for all the nonuronic aldehyde groups at ends of chains, and on the more ready breakdown of oxycelluloses produced by peroxide oxidation. This conclusion is based also on the fact that the splitting of glycols by hydrogen peroxide with formation of two aldehyde groups has been demonstrated for the simplest glycols and follows also from our experiments on the oxidation of methyl glucoside. There are therefore grounds for explaining the facts that we have given from the point of view of this reaction in the case of the oxidation of cellulose with hydrogen peroxide. Nevertheless, such an explanation does not exclude the possibility of the occurrence of other processes leading to similar changes in the oxycelluloses.

In complete absence of catalyst, the oxidation of cellulose by hydrogen peroxide at about 50° proceeds extremely slowly and is qualitatively different from oxidation in presence of Fe^{++}. Very few oxidized groups are formed, and practically all of the carboxyls formed are uronic. Nevertheless, chain-breakdown occurs after a time. Prolonged oxidation with hydrogen peroxide in absence of catalyst leads, therefore, to a fall in viscosity without any appreciable accumulation of functional groups.

SUMMARY

1. A study has been made of the composition of oxycelluloses obtained by oxidation with hydrogen peroxide in acid, neutral, and alkaline media.

2. It has been shown that chemical modification of the cellulose and fall in degree of polymerization occurs at all values of pH, though in varying degree: oxidation proceeds most intensively in strongly alkaline ($pH > 11$) and in acid ($pH < 4$) media.

3. In the oxidation of cellulose by hydrogen peroxide the same chemical processes occur as in the oxidation of the simplest sugars, namely: the primary OH groups are oxidized to aldehyde and carboxyl groups; secondary OH groups are oxidized with formation of ketone groups and oxidation of 2,3-glycol groupings with rupture of the ring yielding two aldehyde groups, which may be converted further to carboxyls.

The introduction of a catalyst(Fe^{++}) accelerates the oxidation processes, particularly those leading to rupture of the pyran ring with formation of nonuronic carboxyls.

4. Certain differences are to be observed between the chemical compositions and properties of oxycelluloses obtained by hypochlorite and by peroxide oxidation. The most important cause of these differences appears to be the breakdown of the glycol grouping into two aldehyde groups, a reaction that has not yet been shown to occur in oxidation with hypochlorites.

5. Owing to the occurrence to a marked extent of the latter type of oxidation with rupture of the pyran ring, the variety of new functional groups formed in the cellulose macromolecule during its oxidation by hydrogen peroxide is even greater than in hypochlorite oxidation: under all pH conditions groups will be formed that reduce the stability of the glucoside linkages in acid and alkaline media and so induce chain-breakdown.

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Institute of Organic Chemistry of the
USSR Academy of Sciences

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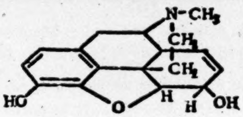
* See Consultants Bureau English translation, page 199.

ALKALOID CHEMISTRY — ITS SIGNIFICANCE, AND ITS IMMEDIATE PROBLEMS*

V. M. Rodionov

The term "alkaloids", proposed in 1818 by Meisner for vegetable bases of complex structure that have powerful physiological effects, quickly received general acknowledgement, for it was in accord with the requirement that new substances should be characterized by their most important attribute. In this case the most important characteristic of the new compounds appeared to be their well marked alkaline properties. Study of the reactions and structures of alkaloids has been of tremendous importance for the development of theoretical and preparative organic chemistry, and it has created several new sections in this subject. The following examples will serve sufficiently well to demonstrate this point.

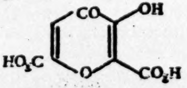
At the very beginning of the nineteenth century, the first alkaloid, morphine (I) was isolated from opium:



Study of the properties of morphine showed that the characteristic pharmacological sedative action of opium is due essentially to the presence therein of morphine. It was by this means that it first became possible to carry out quantitative investigation of the physiological efficiency of this drug. The discovery of such an active compound as morphine was of great significance and gave rise to many investigations of other drugs of vegetable origin and also of the plants themselves.

In 1820 a method was published for the isolation of quinine and cinchonine, the main active principles of another, still more important medicinal preparation — cinchona bark, used in the treatment of malaria. The study of opium and cinchona bark very soon showed that these preparations are complex mixtures of vegetable bases that are fairly similar in structure and that the overall biological and medicinal actions of opium and cinchona bark are in many ways different from those of the individual substances morphine and quinine.

This important observation led to a deeper investigation of the starting materials; methods of isolation and of the further separation of the component parts (the so-called subsidiary alkaloids) were refined, and it was found that each of the complex medicinal preparations, opium and cinchona bark, contain more than 25 different individual substances, sometimes with similar, and sometimes with quite different, physiological properties. The common property of all these compounds was their basic character — the propensity for stable salt formation with both mineral and organic acids. Almost all of the alkaloids that have been isolated from plants are there present as salts, sometimes of very characteristic organic acids: meconic for the opium alkaloids (II), quinic for the cinchona bark bases (III), etc.



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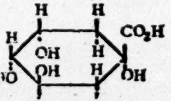

(III)

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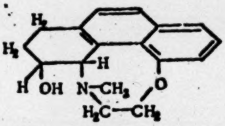
* Paper read before a combined session of the Division of Chemical Sciences of the USSR Academy of Sciences and the UzbekSSR Academy of Sciences on October 25th, 1952 in Tashkent.

The investigation of the chemical composition of opium and cinchona bark led to extensive investigation of plants, particularly poisonous plants, with respect to their content of alkaloids. The number of such compounds began to grow rapidly and has now attained a very large value (more than 1200 individual substances).

The careful study of the properties and structures of the alkaloids isolated has been found to be particularly valuable and important for the chemistry of heterocyclic compounds. This complicated branch of organic chemistry owes its early successful development largely to results obtained in the investigation of various alkaloids. A very large number of important syntheses were the results of early attempts to make an approach to the syntheses of morphine and quinine. The preparation, for example, of such an interesting heterocyclic compound as morpholine (V) was prompted by the desire to confirm one of the early incorrect formulas proposed for morphine (IV):

(Knorr, 1903).



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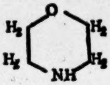
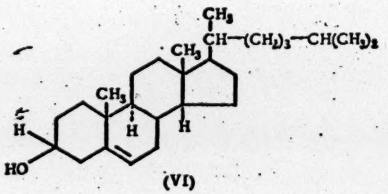


(V)

Morpholine was later found to be a very valuable starting material for the preparation of pharmacological preparations, and also for the synthesis of some basic dyes (Rosol Red and Scarlet).

The establishing of the phenanthrene ring system as the basis of the morphine molecule resulted in an exhaustive study of the properties of phenanthrene itself and of its derivatives, several general syntheses of these substances being developed at the same time. This made it possible later to determine the structures of the biologically important sterols, which include compounds such as cholesterol (VI), coprosterol, phytosterol, ergosterol, vitamins of the D group, bile acids, sex hormones, hormones of the adrenal cortex, digitalis glucosides, and many others. Investigations in this field led to the synthesis of many valuable preparations of the sex hormone type and also, quite recently, to the elucidation of the structure and to the synthesis of such an important medicinal preparation as cortisone (VII)*.



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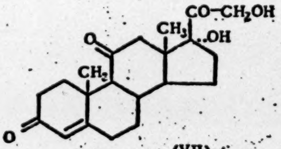

(VII)

Already immediately after the discovery of the vegetable bases, systematic work began on the preparation of active substances that could replace morphium and other alkaloids. Such attempts were completely successful in many cases, and some of the preparations synthesized (for example, demerol and its analogs, also compounds of the 4-piperidinol type, particularly Soviet promedol**) are considerably more active as sedatives than morphine, and may displace morphine and pantopon, for preliminary investigations indicate that they are not habit-forming. In this respect, caution is necessary, for over-enthusiasm for certain new drugs has frequently reacted unfavorably on treatment. It will be sufficient to refer to the many unpleasant consequences of the incorrect use, at one time, of the drug sulfidine and, possibly of sulfamide drugs in general; they are frequently taken without suitable medical advice.

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* Cortisone is able to relieve suffering due to rheumatic arthritis, rheumatic fever, and such severe infections as pneumonia, it is, at the present time, one of the most extensively studied drugs.

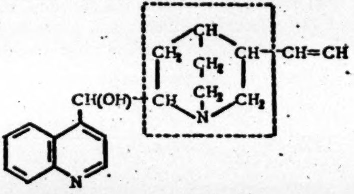
** Synthesized by I. N. Nazarov (Institute of Organic Chemistry of the USSR Academy of Sciences).

Feverishly hasty application of new discoveries is very characteristic of our times, a statement that is true, of course, not only of drugs. The typical attitude to new things in the last century was quite different. For the purpose of comparison we will take two examples. In 1784 the first patent for puddling was taken out, and in 1818 the technical difficulties of the process were overcome by the invention of a suitable hearth, and more vigorous propaganda for the desirability for puddling was begun, but only in 1849, i.e. 65 years after the discovery of the method, did the process come into regular use.

A similar example may be cited from the manufacture of pharmaceuticals. In 1860 a method for the preparation of salicylic acid was discovered, and in 1873 all the technical difficulties had been overcome and the synthesis of this important medicinal and technically necessary product was introduced into industry. Nevertheless, toward the end of the nineties of the last century it was still possible to find statements in pharmaceutical literature to the effect that certain derivatives of synthetic salicylic acid are inferior with respect to quality and physiological action to the natural compounds. This cautious attitude has now completely changed: quite frequently in foreign countries, a newly discovered article will be sold before it has been carefully tested and shown to be sound, and a new drug is sometimes put into use without even a preliminary clinical test.

The study of the subsidiary opium alkaloids contributed a great deal to the development of isoquinoline chemistry, and syntheses were worked out for many natural alkaloids: papaverine, narcotine, narceine, and others. The difficulty encountered in the elucidation of the structural formula of morphine itself is particularly worthy of note. Almost 130 years were required for the precise determination of the structure of the complex and labile molecule of this important alkaloid, and only quite recently has the total synthesis of this compound, which confirmed the structural formula proposed for it in 1935, been effected.

Of no less significance for the development of the chemistry of heterocyclic compounds and of medicinal products was the study of the structure of quinine (VIII) and subsidiary alkaloids derived from cinchona bark.



(VIII)

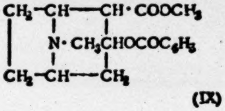
(R = H in cinchonine and OCH_3 in quinine. The quinuclidine ring system is indicated by the broken line.)

The chemistry of two very important heterocyclic systems, quinoline and quinuclidine, was brought into being. These two compounds form the basis of many medicinal preparations. Among the derivatives of quinoline it is sufficient to mention plasmocide, plasmochin, and atophan. Valuable drugs are obtained also from quinuclidine. The preparation of this last compound is of interest, for it made possible one of the most brilliant syntheses of recent times: the synthesis of optically active quinine, in no way different from the natural product.

It may be appropriate here to pass an opinion on the practical value of such brilliant syntheses as those of quinine and morphine. While we have readily accessible natural sources for these compounds — for example, opium and cinchona bark, containing up to 10% or more of these alkaloids, which are readily isolated — the question of the practical expediency of the synthetic preparation of quinine and morphine is scarcely worth thinking about. In this case nature works more cheaply, and it is senseless to compete with it. The question of the improvement of natural preparations by synthesis must, however, be regarded quite differently. Great efforts have been made by many workers to eliminate the bitter taste of quinine, while preserving its antimalarial properties. This was achieved completely by the preparation of euquinine and aristoquine. Interesting work has been done also on the synthesis of ethers of morphine and cupreine, resulting in such important products as codeine, dionine, optichine, etc. It is worthy of mention that the preparation of codeine from morphine has been known for a considerable time, but only in the twenties, in our own country, was the best synthesis for this alkaloid found.

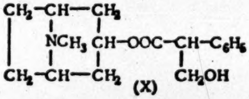
Early attempts to synthesize quinine, the structure of which had not been established, gave industry synthetic dyes, and an attempt to prepare this substance by another method resulted in methods for the preparation of pyrazolone derivatives, which have attained considerable importance for pharmacological chemistry (antipyrine, pyramidone, analgine, etc.) and also for the preparation of fast yellow and red dyes.

The examples cited are sufficient to show what influence the study of these two very important alkaloids has had on the development of preparative organic chemistry, particularly that associated with the synthesis of medicinal substances, but it will be of value to consider yet another alkaloid namely cocaine (IX):



(IX)

The investigation of the structure and properties of this preparation, which was so highly valued by the Peruvian Indians, has formed the basis for the syntheses of anesthetic substances that can replace cocaine; these possess its high qualities, but not its harmful effect on the nervous system. It was found that for a compound to have a local anesthetic action both a substituted amino group and an acylated (generally benzoylated) hydroxy group must be simultaneously present in the molecule. The numerous important preparations of this type include anesthine, alipine, stovaine, dolantin, and naphthocaine. At the same time the peculiarities of molecules having mydriatic and antispasmodic action were established [atropine (X), homatropine, eumydrin, etc.]. Homatropine is the mandelic ester of tropine, and eumydrin is the quaternary methonitrate of atropine:



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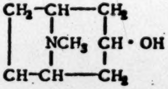
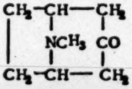


Tropine

Questions concerning the nature of the alkaloids and their functional significance in the life of plants have given rich material both for chemical investigations and for investigations of a botanical and physiological nature. Investigations into phytochemical synthesis are particularly interesting: they show that many complex heterocyclic systems can be synthesized under conditions approximating to those found in nature — at ordinary temperature and pressure, making use only of changes in the pH of the medium. Many very important compounds have been prepared by this method: it will be sufficient to mention such interesting and important substances as tropinone (XI), the starting substance for the synthesis of tropinone derivatives, and lobelanine (XII) (stimulatory substance):



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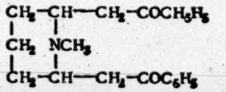


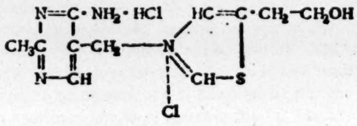
(XII)

From what we have said, a clear picture will be formed of the influence that study of alkaloid chemistry has had on the development of organic chemistry — an influence that has not lost its significance even now: in fact, in many countries at the present time intensified study of new alkaoid-containing plants is proceeding with the object of separating their biologically active principles. It should be mentioned here that our own country is taking a very active part in this work: the work of our investigators has made a considerable contribution to this branch of organic chemistry, and the richness of our flora gives promise of many further successes.*

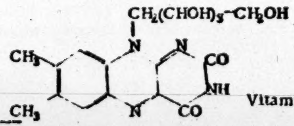
It will be seen from this short sketch that, as a result of investigations into alkaloid chemistry, a large amount of material has been obtained which has contributed much that is necessary and useful for the development of theoretical organic chemistry and for the development of new pharmaceutical substances. However, many important questions still remain unsolved. There is still no generally held opinion concerning the functional significance of alkaloids for the plant. The elucidation of this important matter demands much coordinated work of a profound nature by chemists and physiological botanists. The attempts, as yet very modest, to study the presence of alkaloids during various growing periods of the life of the plant must be continued.

Apart from theoretical importance, these investigations may also have a practical result: they will establish the time at which an important alkaloid may be isolated in the greatest possible yield, and the part of the plant from which it should be obtained. The work on the phytochemical synthesis of alkaloids or heterocyclic systems in general is very important, for it may supply the key to the understanding of the way in which these complex substances are synthesized in the living organism.

An enormous number of isolated alkaloids have still not been sufficiently investigated from the chemical and biological points of view. The structures of many preparations that have long been in use in medicine have not been completely elucidated. Many of these substances have not been studied thoroughly from the pharmacological side. A medicinal preparation that is very valuable for the treatment of one pathological condition may be harmful in another respect. Precipitant application of new drugs is not a rare occurrence. Often, the study of the biological action of the complex of active principles in a plant is inadequate. Whereas at the end of the Eighteenth Century the presence of vegetable acids was regarded as characteristic for a plant, since the beginning of the Nineteenth Century considerably less attention has been devoted to the acid composition of alkaloid-bearing plants, and, at the best, in studies of the compositions of these plants, the vegetable acids have been isolated, their elementary analysis has been made, in some cases they have been synthesized, and nothing further has been done. It is necessary to study the acid composition also from the biological point of view. It is difficult to believe that these substances are indifferent for the life of the plant and for the living organism. It is quite possible that they will be found to be important both from the biological and from the pharmacological point of view. It should be remembered that such acids as nicotinic, pantothenic, p-aminobenzoic, ascorbic, and even some acids of the aliphatic series, have been found to possess vitamin character. It must not be forgotten that many branches of chemistry are closely interwoven, and if new terms, such as vitamin and antibiotic, had not been introduced into chemistry, then compounds such as vitamins of the B, B_1, B_2, and B_6 groups, and antibiotics such as penicillin, streptomycin, and even chloromycetin, would have been included in the alkaloid groups.



(Vitamin B_1)



Vitamin B_2 (riboflavin)

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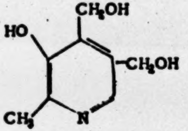
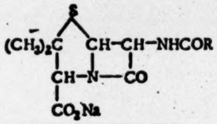
* The investigations of our workers into the chemistry of alkaloids are very extensive and varied; they should be considered in a special article.

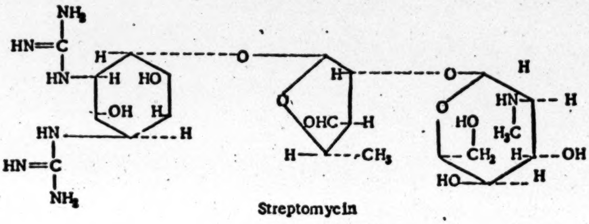

CH₂OH
HO
CH₂OH
CH₃
N

Vitamin B (pyridoxine, adermin)

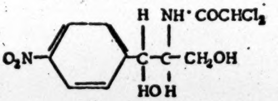
Antibiotics


S
(CH₃)₂C
CH–CH–NHCOR
CH–N—CO
CO₂Na

Penicillin


NH₂
HN=C
HN
H
H
HO
OH
H
HN
H
HN=C
NH₂
O
H
O
OHC
H
H
CH₃
O
H
O
HN
H
HO
H₃C
CH₂
H
OH
HO
H

Streptomycin


H NH·COCHCl₂
O₂N
C–C–CH₂OH
HO H

Chloromycetin (chloramphenicol)

For the investigators of our country who are working on questions in alkaloid chemistry there is a very large number of problems that remain unfinished, or have not yet been tackled. Also, the investigation of the alkaloid-bearing plants of our Central Asian republics is not completed. The same may be said concerning our central regions: by way of example it may be pointed out that up to now inadequate investigation has been given to plants of the greater celandine type, to hellebores, and to many others that are characteristic of the central belt of European Russia. There is also an enormous wealth of plants in the Far East and the Ussury province which await their turn and have as yet received practically no attention

The possibility of propounding and solving such difficult problems is becoming ever greater, for with every year the more remote regions of our fatherland become more and more enriched in universities and research institutes.

BRIEF COMMUNICATIONS

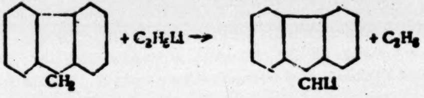
CRYSTALLINE ORGANOLITHIUM COMPOUNDS.

9-FLUORENYLLITHIUM. PHENYLETHYNYLLITHIUM.

T. V. Talalaeva and K. A. Kocheshkov

The method we have developed [1], for the preparation of crystalline ethyllithium and, therefore, of pure solutions of this substance, free from extraneous matter, has found wide application for the preparation of crystalline aromatic organolithium compounds [2], and aralkyl compounds [3], by metal—metal, or metal—halogen replacement with organoantimony, organobismuth, and halogen-substituted compounds.

In the present investigation on the preparation of crystalline fluorenyllithium and phenylethynyllithium, the reaction of hydrogen—metal exchange (the Shorygin reaction) was used [7]:



The metalation of fluorene by ethyllithium (in benzene and ligroin) has been described previously and did not lead to the isolation of individual fluorenyllithium; the authors [4] gave neither the yield nor the analysis of the substance. The reaction of ethyllithium in ether solution (in which it is rapid) [5] and in xylene [6] (18 hours, 80% yield) has been described; again no crystalline substance was isolated. Hence, as we were carrying out a systematic study of crystalline organolithium compounds, we considered it necessary to obtain an individual preparation of fluorenyllithium (a representative of the cyclopentadiene—fluorene group of compounds [7]). Still less is known of isolated representatives of the acetylene series. The formation of phenylethynyllithium in ether solution from phenylacetylene and butyllithium (or phenyllithium) has been demonstrated indirectly by the formation of phenylpropiolic acid. In the present investigation we have prepared crystalline phenylethynyllithium and described its properties:

$$C_6H_5 \cdot C{\equiv}CH + C_2H_5Li \rightarrow C_6H_5 \cdot C{\equiv}CLi + C_2H_6.$$

All operations in the preparation of crystalline fluorenyllithium and phenylethynyllithium were carried out under the conditions and in the apparatus that have been described previously [1, 2, 3].

EXPERIMENTAL

9-Fluorenyllithium

Ethyllithium (1.15 g; 1 mol.) in benzene (30 ml) was introduced into the apparatus previously described [2], and a solution of fluorene (5.5 g; 1 mol. + 0.2 g excess) in hot benzene (15 ml) was added. Immediately on mixing the solutions, there was an orange coloration and evolution of ethane. The reaction proceeded on its own at room temperature (23-24°) for seven hours (steady evolution of gas). Orange crystals of fluorenyllithium separated. In order to complete the reaction the mixture was heated at 75-78° for 3 hours 30 minutes, until ethane ceased to be evolved. The warm solution was filtered under nitrogen. The residue was washed on the filter, once with benzene and three times with dry pentane, was dried in a stream of nitrogen (in the apparatus already described [2]), and was sealed in tubes. The yield was quantitative.

Found %: Li 3.68; 3.82
$C_{13}H_9Li$. Calculated %: Li 4.03

Crystalline fluorenyllithium is a yellow substance having a slight orange tinge; it is soluble in ether and difficultly soluble in benzene and hexane. It is infusible, does not inflame in air, but is readily decomposed with decolorization. It may be preserved unchanged for at least a year when sealed in tubes under pure dry nitrogen.

It gives a strong test with Michler's ketone (it is most convenient to take ether solutions of fluorenyllithium).

Phenylethynyllithium

Ethyllithium (0.49 g; 1 mol.) in benzene (13 ml) was placed in the apparatus (described previously [2]). A dropping funnel was attached to the apparatus, and from this, with shaking, phenylacetylene (1.5 g. 1 mol.) was added gradually. A vigorous reaction ensued, with rise in temperature, evolution of ethane, and formation of a white precipitate of phenylethynyllithium. The reaction rapidly came to an end. The apparatus was left until next day, when the precipitate was filtered off under a pressure of nitrogen (this filtration must be carried out on a wide porous-glass filter, as it is otherwise very slow). The precipitate was washed three times with pentane, dried at 35-45° for one hour in a stream of nitrogen, sealed in tubes, and analyzed. The yield was quantitative.

Found %: Li 6.40; 6.41
C_8H_5Li. Calculated %: Li 6.43

Crystalline phenylethynyllithium is a white infusible substance. In air it does not inflame, but it rapidly decomposes. It is soluble in ether, difficultly soluble in benzene or hexane. It reacts vigorously with water and with alcohol. It gives a color reaction with Michler's ketone.

SUMMARY

1. The hydrogen—metal exchange reaction (Shorygin's reaction) has been employed for the synthesis of crystalline fluorenyllithium from fluorene and ethyllithium.

2. The same reaction has been used for the synthesis of crystalline phenylethynyllithium from phenylacetylene and ethyllithium.

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[3] T.V. Talalaeva and K.A. Kocheshkov, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 2, 290 (1953).**

[4] W Schlenk, E. Bergmann, Ann., 463, 192 (1928); O. Blum-Bergmann, Ann., 484, 36 (1930).

[5] K. Ziegler, L. Jakob, Ann., 511, 45 (1934).

[6] H. Miller, G. Bachmann, J. Am. Chem. Soc., 57, 766 (1935).

[7] K.A. Kocheshkov and T.V. Talalaeva, Synthetic Methods in the Field of Lithium, Sodium, Potassium, Rubidium, and Cesium Organometallic Compounds, Acad. Sci., U.S.S.R Press, 1949, p. 67.

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L. Ya. Karpov Physicochemical Institute

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* See Consultants Bureau English translation, page 113.

** See Consultants Bureau English translation, page 293.

OBITUARY

ACADEMICIAN VLADIMIR ALEKSANDROVICH KISTYAKOVSKY

On October 19th, 1952, the death occurred, after a severe illness, of Academician Vladimir Aleksandrovich Kistyakovsky, one of the founders of modern physical chemistry and a distinguished scientist who has enriched chemical science by many original and profound investigations and who has trained several generations of workers in science and technology. He was in his eighty-eighth year.

The beginning of V.A. Kistyakovsky's scientific activities practically coincided with the birth of the theory of electrolytic dissociation, and his further work contributed in an exceptional degree to the development of several very important fields of physical chemistry, particularly electrochemistry.

V.A. Kistyakovsky gave an original theoretical treatment of chemical reactions in solution and established laws relating to the capillary rise of liquids at their boiling points. The investigations of Vladimir Aleksandrovich on complex cations, on methods of determining electrode potentials, on the passivity and corrosion of metals, and in colloid chemistry, photochemistry, and stoichiometry; his formulas for latent heats of vaporization and for the dependence of vapor pressure on pressure at near the boiling point; and his various other works—all these will remain for ever in the treasure house of science.

The development of the film theory of the passivity of metals, which was originated by V.A. Kistyakovsky in 1909, led him to the formulation in 1925, of an original film theory of metal corrosion, which has shown itself to be reliable means of ascertaining the essential features of the complex phenomena of metal corrosion and has given clear indications of the directions to be taken by future investigations in this field.

At the basis of V.A. Kistyakovsky's film theory lies the hypothesis that a metal surface in moist air is covered by a film. The structure of this film is different for different metals: it varies from a molecularly adsorbed layer to a layer of oxides, in the case of readily oxidizable metals. The transition of a metal from the passive condition (in which it has a continuous surface film of oxides) to the active state is associated with the appearance of pores in the film and is not conditioned necessarily by the complete removal of the oxide film from the surface.

The corrosion of metals in moist air and in solutions of electrolytes (if oxides can exist under the conditions under which the process is carried out) proceeds mainly on account of local currents flowing between parts of the oxide film, occlusions in the surface of the metal, and the metal itself. Oxygen and carbon dioxide serve as depolarizers for the local currents.

V. A. Kistyakovsky regarded the rusting of iron in a profoundly dialectical fashion, treating it as a complex process in the course of which the local currents break up the film, forming pores. Molecular forces also free the metal surface from the film, causing the film to come away by bringing about its crystallization. On the other hand, electrical forces re-create the film in the bared places (by means of the process $n\,Fe + m\overline{OH} \rightarrow Fe_n(OH)_m + mE$). The process proceeds continuously: in effect we have disruption of the film, its crystallization, and erosion of the iron at the anodes of the local currents; and rust therefore accumulates.

The further advance of science, armed with new and ever more perfect methods of investigation, does not lead to the rejection of V.A. Kistyakovsky's film theory of metal corrosion, but, on the contrary, leads to its consolidation and to a call for its further development.

V.A. Kistyakovsky's investigations have always been devoted to the theoretical and experimental study of questions having great significance for the national economy of the U.S.S.R. He published more than 120 papers of the highest scientific importance during more than sixty years of scientific activity.

In 1916 V.A. Kistyakovsky published the first Russian textbook on electrochemistry; it was packed with new ideas and original methods. In 1926, V.A. Kistyakovsky's textbook, "Applied Physical Chemistry" was published.

The scientific services of V.A. Kistyakovsky were marked by his election in 1925 as Corresponding Member and in 1929 as Active Member of the U.S.S.R. Academy of Sciences.

In the Laboratory for Colloids and Electrochemistry and the Institute for Colloids and Electrochemistry of the U.S.S.R. Academy of Sciences (founded by V.A. Kistyakovsky and directed by him until 1939), Vladimir Aleksandrovich with his students and collaborators, carried out extensive investigations on metal corrosion and electrocrystallization. After the conversion of the Institute for Colloids and Electrochemistry into the Institute of Physical Chemistry of the U.S.S.R., Vladimir Aleksandrovich directed the Laboratory for Colloids and Electrochemistry in this Institute until his death, so acting as leader of scientific work on passivating films on metals and on the motoelectric phenomena of potential changes at electrodes resulting from their movement in electrolyte solutions.

Vladimir Aleksandrovich Kistyakovich began his activity as a teacher in 1897, at St. Petersburg University, where, for the first time in Russia, he gave lecture courses in electrochemistry and photochemistry. During his period at the St. Petersburg Polytechnical Institute, he instituted the first big laboratory in Russia devoted to work on physical chemistry and electrochemistry.

During his teaching career (1897-1934), Vladimir Aleksandrovich trained many hundreds of metallurgists and chemists, to whom he lectured on physical chemistry, electrochemistry, thermodynamics, and inorganic chemistry.

From 1934 to 1939, V.A. Kistyakovsky was a member of the Moscow Soviet of Worker-Peasant and Red-Army Deputies.

The government of the U.S.S.R. set a high value on V.A. Kistyakovsky's services to science and rewarded him on two occasions with the Order of Lenin.

Vladimir Aleksandrovich Kistyakovsky, scientist patriot, devoted son of the Fatherland, has, by his sixty years of scientific activity, and his forty years of fruitful work, devoted to the preparation of cadres of scientific and technical workers, shown an example of self-effacing and fruitful service to science and to the Fatherland.

The bright image of V.A Kistyakovsky will live on in the hearts of all who knew him to the ends of their days. Vladimir Aleksandrovich Kistyakovsky's scientific ideas will, for a long time yet, continue to encourage the further development of physical chemistry, and his name will be preserved forever in the history of Soviet chemistry.

CURRENT EVENTS

AWARD OF D. E. MENDELEEV PRIZES FOR 1952

The Presidium of the U.S.S.R. Academy of Sciences has awarded D.E. Mendeleev prizes for the 1952 contest as follows.

A prize of 20,000 roubles to G.V. Akimov, Corresponding Member of the U.S.S.R. Academy of Sciences, E.N. Paleolog, Candidate of Chemical Sciences, and G.B. Klark, Candidate of Technical Sciences, for a series of investigations on the electrochemistry of protective films on metals.

A prize of 10,000 roubles to G.S. Zhdanov, Doctor of Physicomathematical Sciences, and Z.V. Zvonkova, Candidate of Chemical Sciences, for the work, "The Crystal Chemistry of Metal Thiocyanates".

A prize of 10,000 roubles to A.B. Nalbandyan, Doctor of Physicomathematical Sciences, and V.V. Voevodsky, Candidate of Physicomathematical Sciences, for the work, "The Mechanism of the Oxidation and Combustion of Hydrogen."

A prize of 10,000 roubles to A.M. Rubinshtein, Doctor of Chemical Sciences, for the work, "The Physical Structure and Properties of Catalysts for Organic Reactions".

The investigations of G.V. Akimov, Corresponding Member of the U.S.S.R. Academy of Sciences, and his co-workers on the electrochemistry of protective films on metals are of great scientific and practical importance. The question of the nature of oxide films, which is extremely important for the theory of metal corrosion, has been approached from entirely new angles in G.V. Akimov's investigations. The great effect of surface oxide films on the rate of metal corrosion has been known for a long time. This phenomenon was first investigated and described by M.V. Lomonosov in his work on the action of nitric acid on iron. The fruitful work of the late Academician Kistyakovsky and of the late Professor P.D. Dankov, on protective films leading to the creation of the film theory of corrosion, comprises an important stage in the study and estimation of the significance of oxide films on the corrosion behavior of metals.

In the investigations entered for the contest, which were carried out in conjunction with G.V. Klark and E.N. Paleolog, G.V. Akimov developed the idea of the electrochemical heterogeneity of protective films, proved this hypothesis experimentally, and presented many important facts of scientific and practical value.

The investigations were carried out by elegant electrochemical methods: in many cases novel apparatus, constructed by G.V. Akimov and his co-workers, was used.

In the paper, "Introduction to the Electrochemistry of Protective Films", which was published in "Progress of Chemistry", Vol. 16, No. 3, p. 353 (1947), G.V. Akimov rejected W. Müller's concept of the oxide film on a metal as a normal microgalvanic system. He exposed the fundamental error made by Müller, namely the consideration of only the ohmic resistance of the system and complete neglect of polarization.

On the basis of the results of experimental investigations carried out in conjunction with E.N. Paleolog, G.V. Akimov developed the concept of the electrochemical structure of protective films and of the presence on them of regions of three sorts: cathodic, anodic, and electrochemically neutral. By means of these investigations a new branch of corrosion science was discovered: the electrochemistry of protective films.

Among the succeeding investigations of G.V. Akimov and co-workers, that carried out, in conjunction with E.N. Paleolog on the electrochemical structure of protective films on metals (State Defense Press, 1950), presents great scientific interest. In the course of this work the authors developed a simple method for detecting the electrochemically active regions of the protective film. They made use of the principle of cathodic polarization of the samples in a solution containing a special indicator, which revealed quite clearly that a phosphate film on iron may be divided into cathodic, anodic, and inert regions. This work is not only of scientific interest, but also of great practical interest.

Further investigations of G.V. Akimov and E.N. Paleolog (Transactions of the Institute of Physical Chemistry of the U.S.S.R. Academy of Sciences, 1951, Collected Volume No. 1), were devoted to a study of oxide films on aluminum (the electrochemical behavior of aluminum in presence of various anions, and the investigation of its electrode potentials), and they discovered a number of laws applicable to this system.

The authors made wide use of the polarization diagram method, which enabled them to discover a number of interesting phenomena. They found that aluminum having an oxide film of low conductivity and immersed in a solution constitutes a microgalvanic system and that the nature of the anions present in the solution may have an important effect only on the anode process. It was shown that aluminum, in presence of SO_4^{--} and NO_3^- ions is very strongly polarized anodically, whereas in presence of halide ions the polarization of aluminum is very slight.

When we consider the contemporary importance of aluminum in aviation and the consequent exceptional importance of studies of the causes of corrosion damage to aluminum and the mechanism of its development, the great practical value of these investigations becomes clear.

The thorough investigations of G.V. Klark and G.V. Akimova described in their "Investigations of Protective Films on Metals by the Conductivity Method" (U.S.S.R. Academy of Sciences Press, 1952), are also of great practical importance. The significance of the extensive experimental material obtained by the aid of the apparatus developed by these authors for the measurement of the resistance of surface films on metals extends far beyond the question of checking the applicability of this apparatus. It presents interest on its own account in relation to the determination of the electrical properties of various films on various metals. For the first time a wide characterization of the physicochemical properties of various films on almost all metals (except the alkali metals) is presented.

It should be noted that among a number of laws discovered by G.V. Akimov and his co-workers, and experimentally confirmed by them, there is the relation observed between the position of the metal in D.I. Mendeleev's periodic system of the elements and the electric properties of the films — in particular, the effect of the film on the electrode potential of the metal.

In "The Crystal Chemistry of Metal Thiocyanates" G. S. Zhdanov and Z.V. Zvonkova have generalized a large volume of experimental material obtained as a result of X-ray investigations of the structures of simple and complex metal thiocyanates and have systematized data on their chemical structures on the basis of chemical bond types.

A number of new facts are given regarding the chemical structures of 1) the thiocyanato group; 2) ionic crystals of metal thiocyanates; 3) molecular thiocyanato compounds; 4) thiocyanato compounds having hydrogen bonds; 5) complex thiocyanates of transitional metals, and also of metals of the second group of the periodic system that are most prone to four-fold and six-fold coordination round the complex forming metal.

On the basis of analysis and comparison of the crystal structures of various metal thiocyanates, and also of cyanides and halides, the authors have established a number of crystallochemical relations that are of great importance for the crystal chemistry of simple and complex inorganic compounds.

The purposeful work carried out by the authors over many years forms an important contribution not only to crystal chemistry, but also to the chemistry of complex compounds.

The monograph of A.B. Nalbandyan and V.V. Voevodsky, "The Mechanism of the Oxidation and Combustion of Hydrogen" gives an exposition of the fundamental concepts of the modern theory of branched chain reactions and also of the method of application of this theory to concrete problems, the oxidation of hydrogen being taken as example. The theory is applied to the setting up and substantiation of the reaction mechanism, the determination of the limits of ignition, analysis of the question of heterogeneous chain rupture, and so on, and the whole of the factual material is analyzed on the basis of these theoretical concepts. Formulas are derived for the dependence of the position of the ignition limits on the treatment given to the walls of the vessel, the composition of the mixture, inert and chemically active additives, the action of light, and additions of free atoms.

The phenomena occurring when a mixture burns within the "peninsular" of ignition (kinetics of the nonstationary process, the period of induction, the sharp rise in the concentration of active particles in the reaction zone), are analyzed. The question of the slow oxidation of hydrogen and its transition into an explosion at pressures near to that of the atmosphere is examined. The dependence of the character of the reaction and of the ignition on the treatment given to the vessel walls is demonstrated and explained, and in particular it is shown that when the explosion is of a thermal nature in clean vessels, in which the rate is very high, then in vessels that have been treated with salts, in which the rate is 100-1000 times lower, the explosion proceeds by chain mechanism. All the experimental data examined in the book are in quantitative agreement with theoretical calculations, and it has been possible to determine with high accuracy the rate constants of all the elementary processes entering into the mechanism of the oxidation of hydrogen. By the use of these values it is possible to calculate beforehand the kinetics of the hydrogen oxidation process in vessels of various form and dimensions (and made of various materials) over a very wide range of pressure and temperature, i.e., to control the oxidation process.

The monograph contains a large amount of experimental material obtained by the authors and it presents a detailed examination and analysis of the whole complex of complicated factors that are characteristic for branched chain reactions. The work is a major contribution to the study of the kinetics and mechanism of chemical reactions.

In A.M. Rubinshtein's "The Physical Structure and Properties of Catalysts for Organic Reactions", an extensive field is covered. The author has studied the relation between the structure of catalysts as revealed by X-rays and their catalytic activity, the dispersity of the sample or the parameters of its crystal lattice (rarely both of these characteristics simultaneously) being determined by X-ray analysis. In individual cases the phase composition was studied also. The greater part of the data refersto the dehydrogenation and hydrogenation of organic compounds on metals (nickel, cobalt, platinum, and palladium).

A number of investigations are devoted to the dehydration and dehydrogenation of alcohols on magnesium oxide, titanium dioxide, and aluminum oxide. A somewhat isolated position is occupied by data on the ketonization of acids on calcium and barium carbonates.

The author has been carrying out these investigations for more than fifteen years. The most systematic study has been devoted to the relation between X-ray dispersity and catalytic activity, and in a number of cases optima have been observed in the microcrystal dimensions and the effect of interatomic distances in the catalysts on their activity and selectivity in organic reactions has been noted.

The investigations are devoted to a problem of present-day importance and fall in with the line of work of the leading school of Soviet organic catalysis headed by Academician N.D. Zelinsky. A.M. Rubinshtein and his co-workers have been responsible for a considerable proportion of the work carried out in the Soviet Union on the X-ray-structure analysis of catalysts.

FROM THE COMMITTEE ON THE DEVELOPMENT OF THE SCIENTIFIC HERITAGE OF A. M. BUTLEROV AND THE PUBLISHING OF HIS WORKS

The committee of the Division of Chemical Sciences of the U.S.S.R. Academy of Sciences on the development of the scientific heritage of A.M. Butlerov and the publishing of his works appeals to all organizations and individuals to inform the Committee of any material in their hands relating to the life and activities of Academician A.M. Butlerov and also to his letters to S.T. Aksakov, P.P. Alekseev, A.I. Bazarov, F.F. Beilstein, N.N. Beketov, P.D. Boborykin, I.A. Bolzani, A. Crum-Brown, F. Vroblevsky, A. Burtz, N.A. Golovkinsky, G.G. Gustavson, A. Ya. Danilevsky, A.M. and K.M. Zaitsev, N.N. Zinin, I.A. Kablukov, M. Ya. Kittary, K.K. Klaus, M.A. Kovalevsky, D.P. Konovalov, N.I. Lavrov, Yu. V. Lermontova, M.D. Lvov, V.V. Markovnikov, D.I. Mendeleev, N.V. Nasonov, F.V. Ovsyannikov, A.N. Popov, I.M. Sechenov, A.V. Sovetov, A.S. Famintsyn, F.M. Flavitsky, A.I. Khodnev, L.N. Shishkov, C. Schorlemmer, A.P. Eltekov, E. Erlenmeyer, A.I. Jacobi and others.

All communications should be sent to the Committee's address (Moscow, B. Kaluzhskaya, 31. The Division of Chemical Sciences of the U.S.S.R. Academy of Sciences).

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THEORETICAL AND EXPERIMENTAL YIELDS OF STYRENE IN THE CATALYTIC DEHYDROGENATION OF ETHYLBENZENE

N. I. Shuikin and I. I. Levitsky

Calculations of the equilibrium constants for the dehydration of ethylbenzene were first published in the literature in 1943 by Guttman, Westrum and Pitzer [1]. These authors point out (without giving numerical data) that their calculated equilibrium values for the extent of dehydrogenation within the range 425-500° are close to the experimental values obtained by Sergienko [2]. At higher temperatures the calculated values are greater than the experimental, which Guttman and his co-workers attribute to the development of side reactions.

However, similar discrepancies between the theoretical and experimental yields of styrene have been utilized in some papers to support the assumption that the dehydrogenation of ethylbenzene does not reach an equilibrium state (or reversibility), and that the yields of styrene are determined only by the reaction velocity. Marukyan studied the dehydrogenation of several alkylbenzenes and established [3] some relationships concerning the connection between the structure of the alkylbenzenes and their relative dehydrogenation rates. This assumption served as a basis for the creation of a new fragment of the multiplet theory, "the quintet mechanism of dehydrogenation" [4], according to which the dehydrogenation of ethylbenzene and the diethylbenzenes takes place at the active center of five atoms ("quintet") when the molecules are densely oriented on the catalyst surface. The basis for the presentation of these concepts was the assumption that the yields of styrene were determined solely by the velocity of dehydrogenation of ethylbenzene. This assumption was prompted by the fact that the thermodynamic calculation provided evidence that equilibrium was not established [3].

Wenner and Dybdal [5] also associated the discrepancies between the theoretical and experimental yields of styrene with the absence of equilibrium. These authors calculated the velocity constant for the dehydrogenation of ethylbenzene from the following equation:

$$\frac{dS}{dW} = k\left(P_{eb.} - \frac{P_{st.}P_H}{K_E}\right)$$

where dS is the amount of styrene produced in 1 hour in a volume element containing dW of catalyst; k is the velocity constant; K_E is the equilibrium constant; $P_{eb.}$, $P_{st.}$ and P_H are the partial pressures of ethyl benzene, styrene and hydrogen in the reaction zone. We shall return to the results of this work later.

In recent years many authors [6,7,8,9] have published data for thermodynamic calculations on the dehydrogenation of ethylbenzene. All these data have been obtained by the method of statistical thermodynamics, and they lead to almost identical equilibrium constants. The work of Ghosh [10] and his co-workers is the only experimental study on the thermodynamic equilibrium of the reaction. In this work the dehydrogenation of ethylbenzene was studied at low pressures (11 to 40 mm Hg) within the temperature range 360 to 495°. The equilibrium constants determined by these authors are greater than those which we have calculated from the data of Vvedensky, Korobov and Frost, Kilpatrick, Rossini and others [6,7,8]. Thus, for example, Ghosh and his co-workers obtained a value of $K_E = 0.031$ at 495°, but our calculated value for the same temperature is $K_E = 0.024$. The difference in the yields of styrene calculated from these values of K_E amounts to only 2% (the corresponding yields are 17.3 and 15.5%).

In our investigation of the mode of action of inert diluents on the catalytic dehydrogenation of ethylbenzene it was established that this reaction reaches a state of thermodynamic equilibrium over a wide range of molar velocities [11]. All the thermodynamic calculations in this investigation were based on equilibrium constants obtained from experimental data, due allowance being made for side reactions (polymerization, cracking). In this work it was also noted that the styrene content of the catalyzation product (obtained at 575°) was 9% less than the theoretical yield.

In the present paper a systematic comparison is made between the theoretical yields of styrene from ethylbenzene and experimental values obtained under the conditions which are ordinarily used for the reaction. These conditions did not exclude the possible development of side reactions, and for this reason the data cannot be used as a basis for checking the equilibrium constants. It should be mentioned that in the literature not only is such a comparison not described, but even values for the theoretical yields of styrene from ethylbenzene are lacking. The calculation of these values is therefore given below.

Calculation of the Thermodynamic Equilibrium for the Dehydrogenation of Ethylbenzene

The equilibrium constants for the dehydrogenation of ethylbenzene were calculated from the equation [12]:

$$R \cdot \ln K_E = -\left(\Delta \frac{F^0 - H_0^0}{T} + \frac{\Delta H_0^0}{T} \right).$$

Here R is the gas constant; $\Delta \frac{F^0 - H_0^0}{T}$ is the difference between the corresponding functions for the reaction products (styrene and hydrogen) and the starting-material (ethylbenzene); ΔH_0^0 is the heat of dehydrogenation of ethylbenzene (cal/mole at 0°K); T is the temperature in degrees K.

Values of the function $\left(\frac{F^0 - H_0^0}{T}\right)$ for hydrogen, styrene, and ethylbenzene were taken from the monograph of Vvedensky [6]. The heat of dehydrogenation of ethylbenzene at zero absolute (ΔH_0^0) was calculated from the heats of formation of ethylbenzene and styrene at the same temperature. The heat of formation of the hydrocarbons (styrene and ethylbenzene) at 0°K was calculated as the difference between the heat of formation at 298°K and the corresponding change in enthalpy $\Delta(H_{298}^0 - H_0^0)$. The enthalpy values of hydrogen, graphite, ethylbenzene and styrene at 298°K and the heat of formation of ethylbenzene at the same temperature were taken from Vvedensky's monograph [6]. The value for the heat of formation of styrene at 298°K was derived from the data of Prosena and Rossini [13].

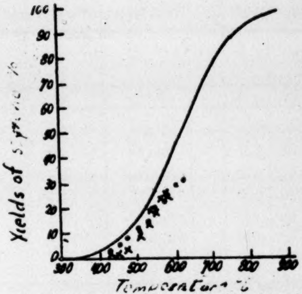
The heats of formation at 0°K calculated in this way were found to be: 13,917 cal/mole for ethylbenzene and 40,340 cal/mole for styrene. The heat of dehydrogenation of ethylbenzene at 0°K is therefore 26,423 cal/mole.

The method we used for calculating the equilibrium constants is of interest, because the heats of formation of the hydrocarbons are the only thermodynamic quantities on which the calculations are based; all the other data needed were obtained by the methods of statistical thermodynamics.

The calculation of the equilibrium yields of styrene from values of K_E was described in our previous paper [11]. Values of K_E for the dehydrogenation of ethylbenzene, calculated in the manner described, and values for the degree of completeness of the reaction at equilibrium are shown in Table I and also on the graph.

TABLE 1
Equilibrium Constants and Values for the Degree of Completeness of the Dehydrogenation of Ethylbenzene

Temperature °C	Equilibrium constant(K_E)	Degree of completeness of dehydrogenation of ethylbenzene,%
127	$5.058 \cdot 10^{-10}$	$2.25 \cdot 10^{-3}$
227	$7.178 \cdot 10^{-7}$	$8.47 \cdot 10^{-2}$
327	$9.683 \cdot 10^{-5}$	0.98
427	$3.296 \cdot 10^{-3}$	5.74
527	$4.732 \cdot 10^{-2}$	21.78
627	$3.784 \cdot 10^{-1}$	52.39
727	2.014	81.74
827	7.870	94.20
927	24.43	98.00



Theoretical and experimental yields of styrene in the dehydrogenation of ethylbenzene — calculated; o – o experimental with $Cr_2O_3-MoO_2-Al_2O_3$; x–x experimental with $V_2O_5-Al_2O_3$.

EXPERIMENTAL

We carried out a study of the dehydrogenation of undiluted ethylbenzene at different temperatures by the method previously described [11]. Two catalysts were studied. Samples of catalyst (up to 50 mm) were not changed in the course of each whole series of experiments, and after each experiment the catalyst was regenerated by means of a stream of air (2 hours at 600°). The results of the experiments with the aluminum-chromium-molybdenum catalyst are shown in Table 2. Column 7 of this table gives values for the theoretical yield of styrene, calculated by the graphical method from the data of Table 1. The discrepancies between the theoretical and experimental yields of styrene are given in column 8. These discrepancies increase from 1.9% at 424° to 21.6% at 627°. The ethylbenzene losses show a corresponding increase from 3.7 to 14.9%. In all the experiments carried out at 424-575° the descrepancy is close to the loss, differing by only 2-3%. This agreement between these values is probably explained by the fact that the discrepancies and the losses are due to the same cause -- polymerization of the styrene produced. The deposition of "tar" was always observed in that part of the catalyzation tube where the product condensed.* At higher temperatures (600-627°) values for the discrepancy are 7% higher than the loss values, which is evidently due to the partial dealkylation of the ethylbenzene starting-material.

The results of experiments carried out with an aluminum-vanadium catalyst are given in Table 3. Up to 475° this catalyst showed a very low activity. However, the styrene yields obtained within the range 525-575° were found to be very close to the corresponding yields obtained with the aluminum-chromium-molybdenum catalyst. The discrepancy and loss values (columns 8 and 9, Table 3) were also close to those described earlier.

The results obtained with these two catalysts are compared with the corresponding theoretical figures on the graph.

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* At its condensation temperature the polymerization velocity of styrene is fairly large, for example, at 150° styrene polymerizes to the extent of 80% in 5 hours. On the other hand, it would be expected that polymerization in the reaction zone would be impossible; at 350-400° polystyrene is completely depolymerized [14].

TABLE 2

Dehydrogenation of Ethylbenzene in the Presence of an Aluminum-Chromium-Molybdenum Catalyst

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
45	424	0.44	3.8	96.3	3.7	5.6	1.9	3.7
46	452	0.44	5.8	96.6	5.6	8.5	2.9	3.4
44	475	0.36	8.8	94.9	8.4	12.0	3.6	5.1
42	503	0.35	11.9	94.6	11.3	16.8	5.5	5.4
43	503	0.97	11.3	97.0	11.0	16.8	5.8	3.0
47	526	0.43	15.1	95.4	14.4	21.7	7.3	4.6
48	551	0.39	20.9	94.6	19.8	27.2	7.4	5.4
49	575	0.41	24.7	92.0	22.7	34.3	11.6	8.0
50	602	0.40	30.8	92.7	28.6	43.0	14.4	7.3
51	627	0.40	36.2	85.1	30.8	52.4	21.6	14.9

TABLE 3

Dehydrogenation of Ethylbenzene in the Presence of an Aluminum-Vanadium Catalyst

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
85	452	0.29	1.5	99.0	1.5	8.5	7.0	1.0
86	475	0.30	3.4	99.0	3.4	12.0	8.6	1.0
91	503	0.31	9.1	98.0	8.9	16.8	7.9	2.0
92	525	0.29	14.7	94.9	14.0	21.7	7.7	5.1
89	551	0.86	17.8	94.5	16.8	27.2	10.4	5.5
103	547	0.24	20.7	87.4	18.1	26.2	8.1	12.6
90	575	1.09	23.9	93.2	22.3	34.3	12.0	6.8
104*	575	1.04	24.8	94.3	23.4	34.3	10.9	5.7
107*	575	1.47	26.3	94.6	24.9	34.3	9.4	5.4
106*	575	1.91	25.4	97.2	24.7	34.3	9.6	2.8
135*	575	2.40	24.7	94.0	23.2	34.3	11.1	6.0

* An earlier [11] calculation of K_E was based on these results.

The results we have obtained are in good agreement with those of Wenner and Dybdal [5]. These authors studied the dehydrogenation of undiluted ethylbenzene in a pilot plant (catalyst volume 350 ml). In Table 4 we give (recalculating for conformity) the results obtained in this work for the temperature range 550-600°. A noteworthy feature is the lack of dependence of the styrene yields on the volume velocity for two to three-fold changes in the latter (compare experiments 232,229, 227); at the same time the styrene yields are very close to those we

TABLE 4

Dehydrogenation of Ethylbenzene in a Pilot Plant: Data of Wenner and Dybdal.

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
228	552	3.29	22.8	88.0	20.1	27.5	7.4	12.0
232	555	1.10	20.9	90.8	19.0	28.3	9.3	9.2
229	555	2.24	23.0	93.2	21.4	28.3	6.9	6.8
227	555	3.47	22.9	96.5	22.2	28.3	6.2	7.5
230	556	2.07	23.0	94.5	21.7	28.3	6.6	5.5
242	598	1.02	26.6	89.1	23.7	42.0	18.3	10.9
239	600	2.03	27.5	90.0	24.7	42.5	17.8	10.0
237	598	3.87	25.2	93.5	23.6	42.0	18.4	6.5

obtained (see experiment 103 and the following ones in Table 3); the equilibrium character of these was established in our previous work [11]. On the other hand, the discrepancies between the theoretical and experimental yields are close to the values for the ethylbenzene losses, which also is in full agreement with our results (compare columns 8 and 9 in Table 4 with the corresponding columns in Table 2). These losses cannot be explained by pyrolysis; in these experiments the authors observed only 0.4-0.8% of benzene and 0.6-1.7% of toluene in the catalyzation product.

It is evident that the authors of this paper were dealing with equilibrium yields of styrene. The equilibrium constants for the dehydrogenation of ethylbenzene calculated from these styrene yields are therefore somewhat doubtful. The results given here, together with those previously given [11], make it possible to assume that the discrepancies between the theoretical and experimental styrene yields are due to the development of side reactions (polymerization, dealkylation). These discrepancies can hardly be cited as proof of the assertion that the dehydrogenation of ethylbenzene does not attain a state of equilibrium; the reaction can attain a state of equilibrium, but side reactions make it impossible to obtain a theoretical yield of styrene.

SUMMARY

1. The extent of dehydrogenation of ethylbenzene at equilibrium has been calculated from thermodynamic data given in the literature. It is shown that the theoretical yields of styrene increase from 5.7% at 427° to 52.4% at 627°.

2. The dehydrogenation of ethylbenzene was investigated at different temperatures. It is shown that in the presence of an aluminum-chromium-molybdenum catalyst the yields of styrene increase from 3.7% at 424° to 30.8% at 627°, but over the same range the discrepancy between the theoretical and experimental yields increases from 1.9 to 21.6%. The activity of the aluminum-vanadium catalyst is low below 525°, but the results obtained at 525-575° are almost identical with those obtained in the corresponding experiments with the aluminum-chromium-molybdenum catalyst.

3. It is shown that values for the discrepancy between the theoretical and experimental yields of styrene are close to the values for the loss of catalyzation product. It is suggested that these discrepancies are caused by side reactions, and they cannot be taken as evidence of failure to reach equilibrium.

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THE EFFECT OF SECONDARY CONSTITUENTS ON THE NATURE OF THE SURFACE HETEROGENEITY OF SOLID BODIES AS SHOWN BY THEIR ADSORPTIVE PROPERTIES

N. M. Manko and V. I. Levin

The adsorptive and catalytic properties of solid bodies are noteworthy because of their extraordinary diversity and specificity. The activity of a solid body in a given process is essentially determined by its nature. In addition, the activity of a definite solid body in relation to one and the same substance varies within very wide limits depending on its present state and on those states through which it has passed in its formation—on its "biography."

Questions dealing with the formation of active surfaces which are closely related to the problem of preparing catalysts having suitable properties, have naturally been the subject of numerous experimental and theoretical studies. In this field, Roginsky has put forward a number of fundamental principles which may be summarized as follows:

1. An active solid body is usually in a state removed from thermodynamic equilibrium. Catalytic activity is connected with the body's excess of free energy over the value of the free energy of the same body in its normal, i.e. thermodynamically stable, state All those conditions which increase the free energy of the catalyst or adsorbent during its preparation must also increase its activity. These hypotheses form what has been termed the supersaturation theory[1-4], and they have been confirmed in a series of experimental investigations[4-7]; they have also been successfully used in the solution of applied problems[8,9].

2. Active bodies which have been prepared in a highly supersaturated state will have structures deviating from normal, and the higher the activity, the larger will be the deviation. These structure deviations or aberrations may include all kinds of purely mechanical defects (lattice voids, structure deformations, etc.). On the other hand, chemical deviations may occur; these include local aberrations in stoichiometric compostion and the intrusion of extraneous substances. From the point of view of catalysis and adsorption, the most stable, and therefore the most important, aberrations are those of a chemical nature [1].

The concept of a relationship between the catlytic activity of a solid body and its secondary constituents is confirmed by all our experience of applied catalysis. This relationship has been studied experimentally in a number of investigations, which have resulted in the establishment of certain laws governing the dependence of activity on the presence of secondary constituents. Experiments have shown that the same secondary constituent can act both as a promoter and as a poison, depending on its concentration. Moreover, a change in the proportion of secondary constituent may result in a change both in the activation energy of the process and in the pre-exponential multiplier of the velocity constant (observed). The group of phenomena associated with the action of secondary constituents on the activity of solid bodies has been termed "modification" [6, 10, 11, 12].

3. The surface of an actual solid body is heterogeneous insofar as its adsorptive and catalytic properties are concerned. This heterogeneity has a profound influence on the character of the laws governing processes which take place at its surface. For the theoretical analysis of heterogeneous-surface processes, a statistical method is used, which has been most fully developed by Roginsky[10,13]. Fundamental to this method is the concept of a distribution function of values of some parameter over area-elements of the surface. This distribution function is a surface characteristic of a given solid body, considered in relation to some definite process.

Most of the experimental applications of the statistical method have been made in the study of activated adsorption [19, 13, 14, 16, 18]. In this case, the surface characteristic used in the distribution function is the adsorption activation energy. The relation between the type of distribution function and the character of the kinetic adsorption equations corresponding to the function, as well as the methods used for deriving distribution functions from experimental data, have already been discussed in sufficient detail [10, 13, 14, 15, 16, 17].

If we start from the idea of a relationship between the activity of a solid body and its content of secondary constituents it is natural to attribute the surface heterogeneity, as shown by its catalytic and adsorptive properties, to the action of these constituents. The formation of some kind of distribution of active centers, according to their degree of activity, must be connected with the presence of secondary constituents of a definite nature and in a definite concentration.

For this reason, experimental and theoretical studies on the effect of admixtures on the character of the surface heterogeneity of adsorbents and catalysts are of undoubted interest.

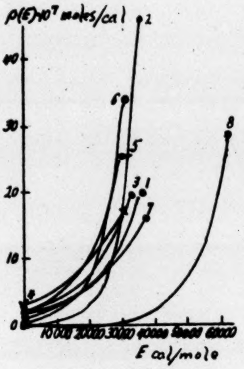

Fig. 1. Graph of the distribution function of surface area-elements for values of the adsorption activation energy of hydrogen on all the carbons studied: 1) ash-containing, 2) purified, 3) with 1% K added, 4) with 1% Ca added, 5) with 1% Pt added, 6) with 1% Ag added, 7) with 1% Ni added, 8) with 1% Fe added.

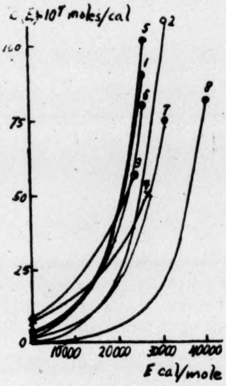

Fig. 2. Graph of the distribution function of surface area-elements for values of the adsorption activation energy of oxygen on all the carbons studied: 1) ash-containing, 2) purified, 3) with 1% K added, 4) with 1% Ca added, 5) with 1% Pt added, 6) with 1% Ag added, 7) with 1% Ni added, 8) with 1 % Fe added.

Experimental studies of this kind can be carried out most simply in the case of the process of activated adsorption. As is known [10,13], the kinetics of activated adsorption on a heterogeneous surface — the process to which the statistical method has been most successfully applied — may be expressed, for defined conditions, by the approximate equation:

$$q(t) = q_{\infty} \int_{E_0}^{E=RT\ln k_0} \rho(E)dE \qquad (1)$$

where $\underline{q}$ is the amount of substance adsorbed up to the time $\underline{t}$, q_{∞} is the amount of adsorbed substance required to form a monomolecular layer on the surface; $\rho(E)$ is the distribution function of area-elements of surface according to value of the adsorption activation energy E, k_0 is the pre-exponential multiplier in the adsorption velocity constant, which is assumed constant over all area-elements; E_0 is the minimum value of the activation energy for the given surface. The function $\rho(E)$ is characteristic of a given adsorbent-adsorbate pair, and from a knowledge of this function, together with the value of k_0 it is possible to derive the kinetic equation for any temperature and pressure of the adsorbate.

The surfaces which have been most studied from the point of view of statistical theory are those of active carbons. The work of Roginsky and his coworkers [14, 10, 10] has shown that the surfaces of active carbons obtained from various sources are heterogeneous with regard to the adsorption activation energy of a number of gases.

Keier and Manko[19] made an experimental study of the effect of the natural ash in a number of technical birch carbons, and also the same carbons with the artificial addition of a series of mineral salts, on the nature of the surface distribution as shown by the adsorption activation energies of oxygen and hydrogen.

In all instances studied the distribution function was found to be of the exponential type.

$$\rho(E) = He^{aE} . \qquad (2)$$

Figures 1 and 2 show graphs of the distribution functions determined by Keier and Manko [19] for the adsorption of oxygen and hydrogen on carbon of varying ash content and with different artificial additives. Differences in the distribution functions for different carbons and adsorbates result in different numerical values of the parameters H and a. However, these parameters are subject to fairly large variations, depending on the nature of the carbon and of the adsorbed substance (see Table 1).

Thus the presence in carbon of mineral constituents, as well as the nature of these constituents, affects the surface heterogeneity, as shown by the adsorptive properties of the carbon. This effect is reflected in a change in the distribution function for the energy of activation. How can this change be expressed? Different distribution functions may be compared on the basis of type (linear, exponential, etc.). This is a purely qualitative comparison, however. Further, surfaces heterogeneous in regard to a given property, x may be characterized by the range of the interval over which this property changes. If we compare among themselves a series of distribution functions, all of the same type $\rho(x)=H$ (uniform distribution), we see that in passing from ρ_5 corresponding to the least heterogeneous surface, to ρ_1, the most heterogeneous function, as shown in Fig. 3, the interval over which the property x for the given surface varies, increases with the degree of heterogeneity. Thus, in the case of a uniformly heterogeneous surface, a characteristic of the degree of heterogeneity is the range covering values of the parameter which has been selected as the independent variable. But in the case of other distributions this interval is not a well-defined characteristic. Indeed, if we compare the two distribution functions shown in Fig. 4, we see that, although both have the same range for the variable x, they differ in their degree of heterogeneity. The function ρ_1 represents a uniformly heterogeneous surface, but the function ρ_2 represents an almost homogeneous one, since the overwhelming majority of the area-elements of this surface have about the same value of the argument x.

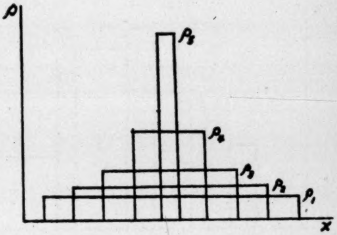

Fig. 3.

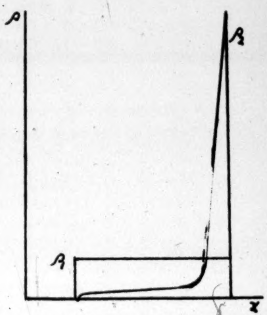

Fig. 4.

On the other hand, in this example (Fig. 3), because of the normal character of the distribution function, the value of the parameter H decreases as the interval for values of x increases. Therefore, for a uniformly heterogeneous surface $\rho(x)=H$ the value of the distribution function H is a measure of the surface heterogeneity. The larger the value of H, the less heterogeneous the surface and the more it tends to homogeneity. In order to extend the treatment to any type of distribution, we consider a surface consisting of a series of uniformly heterogeneous area-elements, for each of which $\rho(x)=H_i$ (Fig. 5). The surface as a whole will be characterized by a mean value $\rho_i(x)$ which is obviously equal to

$$\bar{\rho}(x) = \sum_i \rho_i(x) \frac{s_i}{\sum_i s_i} \tag{3}$$

In this expression $\frac{s_i}{\sum_i s_i}$ is the fraction of the surface in the i-th uniformly heterogeneous area-element. For a surface with an infinite number of area-elements, i.e. for a smooth distribution function, (see Fig. 6), the ratio $\frac{s_i}{\sum_i s_i}$ is replaced by the product $\rho(x)dx$, which characterizes the fraction of area elements of the given type in the case of a smooth distribution function, and the sum (3) is replaced by the integral

$$\bar{\rho}(x) = \int_{x_1}^{x_2} \rho(x)dx\rho(x) = \int_{x_1}^{x_2} \rho^2(x)dx \tag{4}$$

The mean value of the distribution function obtained in this way may be used as a measure of heterogeneity for functions of any type. It is more convenient not to use $\bar{\rho}(x)$, but the reciprocal

$$\epsilon = \frac{1}{\rho(x)}, \tag{5}$$

which we shall term "the degree of surface heterogeneity." By calculating the value of ϵ, we can compare the degree of heterogeneity of different surfaces.

We shall examine in what manner the degree of heterogeneity depends on the parameters of some concrete types of distribution function. In the case of the uniform distribution $\rho(x)=H$ the degree of heterogeneity, according to equation (5) will be equal to

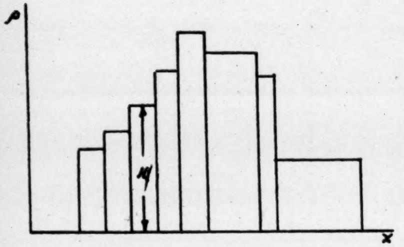

Fig. 5

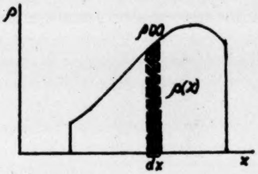

Fig. 6

$$\epsilon = \left[\int_{x_1}^{x_2} H^2 dx \right]^{-1} = \frac{1}{H^2(x_2 - x_1)} \tag{6}$$

But the difference$(x_1 - x_2)$,the interval over which the property $\underline{x}$ varies, depends in its turn on the quantity $\underline{H}$, because of the normal character of the distribution function. Writing the conditions for normalization, we get

$$\int_{x_1}^{x_2} \rho(x)dx = \int_{x_1}^{x_2} Hdx = H(x_2 - x_1) = 1,$$

from which

$$x_2 - x_1 = \frac{1}{H}$$

and consequently

$$\epsilon = \frac{1}{H} \tag{7}$$

Thus, for a uniform distribution the degree of heterogeneity is inversely propotional to the parameter $\underline{H}$, which fully corresponds to Fig. 3.

In the case of an exponential distribution function $\rho(y) = He^{ax}$ we obtain the following expression for the degree of heterogeneity

$$\epsilon = \frac{2a}{H^2[e^{2ax} - e^{2ax_1}]} \tag{8}$$

Further, applying the conditions for normalization,

$$\int_{x_1}^{x_2} He^{ax}\,dx = \frac{H}{a}(e^{ax_2} - e^{ax_1}) = 1,$$

we get

$$e^{ax_2} = \frac{a}{H} + e^{ax_1} \tag{9}$$

From this the degree of heterogeneity will be equal to

$$\epsilon = \frac{2a}{H^2\left[\left(\frac{a}{H} + e^{ax_1}\right)^2 - e^{2ax_1}\right]} = \frac{2}{a + 2He^{ax_1}} \tag{10}$$

TABLE 1

Values of the distribution-function parameters for different carbon surfaces, as shown by the activation energies of hydrogen and oxygen

Carbon	$a\cdot10^4$ mole/cal	$H\cdot10^7$ mole/cal
Adsorption of hydrogen		
Sugar	3.00	—
Birch, deashed (ash content 0.4%)	1.93	0.07
" " plus 1% Ag	1.41	0.5
" " " 1% Fe	1.24	0.01
" " " 1% Pt	0.90	1.9
Birch (containing 3% ash)	0.74	1.4
Birch, deashed plus 1% K	0.72	2.0
1% Ca	0.60	3.0
1% Ni	0.59	1.9
Adsorption of oxygen		
Sugar	6.20	—
Birch, deashed (ash content 0.4%)	1.45	1.4
" " plus 1% Pt	1.43	2.9
" " " 1% Fe	1.40	0.3
Birch (containing 3% ash)	1.25	3.9
Birch, deashed plus 1% Ni	1.21	2.0
" " " 1% Ag	1.20	4.0
" " " 1% K	0.81	9.3
" " " 1% Ca	0.64	8.9

TABLE 2

Degrees of heterogeneity of different carbon surfaces for hydrogen and oxygen adsorption

Carbon	$\epsilon\cdot10^{-4}$ cal/mole
Adsorption of hydrogen	
Sugar	0.67
Birch, deashed (ash content 0.4%)	1.03
" " plus 1% Ag	1.42
" " " 1% Fe	1.61
" " " 1% Pt	2.22
Birch (containing 3% ash)	2.70
Birch, deashed plus 1% K	2.77
" " " 1% Ca	3.17
" " " 1% Ni	3.40
Adsorption of oxygen	
Sugar	0.32
Birch, deashed (ash content 0.4%)	1.38
" " plus 1% Pt	1.40
" " " 1% Fe	1.42
Birch (containing 3% ash)	1.60
Birch, deashed plus 1% Ni	1.65
" " " 1% Ag	1.67
" " " 1% K	2.50
" " " 1% Ca	3.13

If $a \gg 2He^{ax_1}$, approximating, we may put

$$\epsilon = \frac{2}{a}\,, \tag{11}$$

i.e. the degree of heterogeneity is inversely proportional to the exponential index a.

By analogy with what precedes, the degree of heterogeneity of a power distribution function of the type $\rho(x) = H(x-x_1)^n$ may be expressed as follows

$$\epsilon = \frac{2n+1}{(n+1)^{\frac{2n+1}{n+1}}} \cdot \frac{1}{H^{\frac{1}{n+1}}} \tag{12}$$

From expression (10) for an exponential function, it follows that when $a = 0$ the degree of heterogeneity will be equal to $1/H$, as in the case of a uniform distribution, which is clearly obvious, since for $a = 0$ the exponential distribution $\rho(x) = He^{ax}$ reduces to the uniform distribution $\rho(x) = H$. As $a \to \infty$ the degree of heterogeneity reduces to zero, corresponding to an approach toward a homogeneous surface In fact, when $a \to \infty$ the exponential function He^{ax} tends toward the infinite ordinate corresponding to a homogeneous surface.

In the same way, a power distribution reduces to a uniform distribution for $n = 0$ and to a narrow infinite peak, approximating to a homogeneous surface, for $n \to \infty$. In complete agreement with this the degree of heterogeneity ϵ becomes equal to $1/H$ (as for a uniform distribution) when $n = 0$, and tends to zero when $n \to \infty$.

Thus, for a surface having an arbitrary type of distribution the degree of heterogeneity may vary (for a fixed interval of change of the argument $\underline{x}$) from $1/H$, corresponding to a uniformly heterogeneous surface, to zero, corresponding to a surface approaching homogeneity. And in turn the degree of heterogeneity for a uniformly heterogeneous surface may vary from zero ($H \rightarrow \infty$) (homogeneity) to an indefinitely large quantity ($H \rightarrow 0$).

By calculating the value of ϵ, obtained in Equation (5), we can make comparisons between distributions both of the same and of different types with regard to their degree of heterogeneity.

We shall use the method described to determine the degree of heterogeneity of the carbons with different constituents, investigated by Keier and Manko [19]. Calculation shows that for all the samples the inequality $He^{\alpha E_0} \ll \alpha$ is valid; consequently, we may calculate the degree of heterogeneity by the approximate formula (11), making use of the values of α given in Table 1.

The values of the degree of heterogeneity for the adsorption of hydrogen and oxygen on the carbons studied by Keier and Manko [19] are given in Table 2. The data in this table show that the presence of extraneous constituents in the carbons is reflected in the degree of heterogeneity, and this varies with the nature of the constituent and the adsorbed substance.

Comparing the degree of heterogeneity of the carbon "BAU", which contains 3% of ash, with that of the same carbon after its ash content has been reduced by special treatment to 0.4%, we see that in the second case the degree of heterogeneity ϵ is lower both for hydrogen and for oxygen adsorption. The degree of heterogeneity is still lower in the sugar carbons, which have an ash content of a lower order than that of the "BAU" carbon.(Table 3). Thus, the degree of heterogeneity of the carbon, as shown by the adsorption activation energy, increases with the natural ash content.

The degree of heterogeneity is influenced not only by the presence of natural ash, but also by the artificial addition of metals. As will be seen from Table 2, the addition to "BAU" deashed carbon of silver, iron, platinum, calcium or nickel causes an increase in the degree of heterogeneity, though the effect varies with the nature of the additive and with the gas adsorbed. The degree of heterogeneity of sugar carbons also is increased by the introduction of additives, as is shown by Table 4, which has been compiled from the data of Burshtein [20] and of Keier and Manko [19].

TABLE 3

Degree of Heterogeneity of Carbons of Different Ash Content as Shown by Adsorption of Hydrogen and Oxygen

Carbons	Ash content, %	$\epsilon \cdot 10^{-4}$ cal/mole	
		Hydrogen adsorption	Oxygen adsorption
Sugar	0.05	0.67	0.32
Birch, deashed	0.4	1.03	1.33
Birch containing ash	3.0	2.70	1.60

The correlation between the degree of heterogeneity and the amount of extraneous constituents present, which is observed in the case of natural ash constituents, is also found when the extraneous constituents are introduced artifically. Table 4 shows that the degree of heterogeneity of deashed "BAU" carbon with added calcium increases with the calcium content, and the degree of heterogeneity of sugar carbon increases with the platinum content.

The data presented here are not sufficiently extensive to establish a relationship between the degree of heterogeneity and the quantity of extraneous constituent. However, it is clear that the relationship is not a linear one. For low concentrations of the additive (or extraneous constituent), the rate of increase in the degree of heterogeneity is greater than the rate for high concentrations.

Thus, the presence of extraneous additives in carbon affects the degree of surface heterogeneity, causing an increase in all cases. This effect of additives is not peculiar to the adsorption of hydrogen and oxygen, but also occurs with other gases, as will be seen from Table 4, which gives values (calculated from the data of Burshtein [20]) of the degree of heterogeneity for the adsorption of carbon monoxide on sugar carbon, both with and without the addition of 0.2% of platinum.

The degree of heterogeneity of a surface for a given gas is evidently a fairly constant characteristic. The degree of heterogeneity for the adsorption of oxygen on birch carbon (calculated from the data of Reed and Wheeler [21]) was found to be fairly close to the value obtained from the data of Keier and Manko [19] (Table 5). In the case of hydrogen adsorption, values of the degree of heterogeneity calculated from the data of Keier and Roginsky are fairly close to similar values calculated from the data of Burshtein (Table 5).

TABLE 4

Degrees of Surface Heterogeneity of Sugar and Birch Carbons with Various Amounts of Different Additives

Hydrogen adsorption		Hydrogen adsorption*		Carbon monoxide adsorption*	
Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)	Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)	Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)
Deashed birch	1.03	Sugar	0.73	Sugar	0.67
Deashed birch plus 0.01% Ca	2.00	Sugar plus 0.02% Pt	0.96	Sugar plus 0.2% Pt	1.2
Deashed birch plus 0.1% Ca	3.30	Sugar plus 0.2% Pt	0.83		
Deashed birch plus 1.0% Ca	3.34	Sugar plus 1.0% Pt	0.83		

* Data of Burshtein [20]

TABLE 5

Degrees of Surface Heterogeneity of Sugar and Birch Carbons for the Adsorption of Hydrogen and Oxygen, According to Data from Various Sources

Gas adsorbed	Carbon	$\epsilon \cdot 10^{-4}$ (cal/mole)	Reference
Hydrogen	Sugar	0.67	Keier and Roginsky
		0.73	Burshtein [18]
Oxygen	Birch	1.82	Reed and Wheeler
		1.60	Keier and Manko

This analysis of the experimental data on the kinetics of activated adsorption confirms the hypothesis put forward earlier, according to which there is a connection between surface heterogeneity and the presence of secondary constituents on the surface. Since in all cases the introduction of new constituents or an increase in the amount of those already present results in an increase in the degree of heterogeneity, the presence of these constituents is evidently a fundamental cause of heterogeneity. From this point of view it is clear why all the adsorbents investigated were found to be heterogeneous in their adsorptive properties, since it is difficult to imagine the surface of a real solid body completely free of extraneous constituents.

The constancy of distribution type, which was found to be exponential in all cases, is noteworthy. The same type of distribution occurs with carbons containing natural ash, with carbons freed from ash, and with carbons containing artificial additives. The same type of exponential distribution is characteristic of both sugar and birch carbons. Analysis of the data obtained by various authors with various samples at different times points to an exponential distribution of active centers, as shown by the activation energy for activated adsorption. This holds for hydrogen and for oxygen adsorption, and also for the adsorption of other gases, and not only for carbon but also for other adsorbents. This constancy of statistical surface characteristics suggests that there exists some property which is common to all, or most, adsorbents. From what has been said above, this property must be connected with the presence of secondary constituents on the surface.

The insensitivity of distribution type to the nature of the extraneous constituent suggests that for a wide range of substances, the same mechanism governs the action of the extraneous constituent on the distribution, irrespective of the nature of the constituent. In particular, it may be supposed that there is a connection between the distribution of active centers according to activity values and the distribution of individual inclusions according to their size. Moreover, there should be a connection between the inclusion size for a given extraneous constituent and the energy of activated adsorption (as the main characteristic of activity) on the adsorption center associated with this inclusion. With this assumption the constancy of distribution type for the activation energy points to a constant type of distribution for the extraneous constituents, according to the size of the inclusions. The parameters of the latter distribution will vary with variations in the concentration of the constituent, though the distribution type remains unaltered, in the same way as distributions based on the law of chance (Poisson-Gauss distributions). And there will be corresponding variations in the parameters of the distribution for the activation energy.

SUMMARY

1. A method is proposed for the quantitative evaluation of the degree of heterogeneity of distributions which is applicable to distributions of any type.

2. It is shown that the degree of surface heterogeneity of active carbons, as shown by the activation energy for activated adsorption, is dependent on the nature and on the quantity of the secondary constituents. In all cases an increase in the quantity of these constituents results in an increase in the degree of surface heterogeneity.

The secondary constituents have no effect on the distribution type.

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A STUDY OF THE CONDITIONS FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF SILICIC ACID

COMMUNICATION I. METHODS OF DETERMINING SILICIC ACID IN SILICATES BY DEHYDRATING SOLUTIONS OF THE ACID

E. N. Egorova

The gravimetric determination of silicic acid separated from acid solutions is one of the oldest analytical methods. There is an extensive literature on the study of the conditions for the separation of silicic acid from solutions. But, in spite of the large amount of experimental work in this field, the conditions for the complete separation and accurate determination of silicic acid have not been completely elucidated. Many examples of significant errors in the determination of silicic acid, carried out both by classical and by rapid methods, are to be found in practice. These errors occur even when the analytical procedure is technically unimpugnable. The obscurity surrounding the sources of the errors is reflected, evidently, in the different variants of the analytical procedure recommended by different authors.

The generally accepted "classical" method for the determination of silica in silicates consists, as we know, of the following operations:

1. The finely ground silicate sample is fused with sodium carbonate, or with a mixture of sodium and potassium carbonates, and the melt is decomposed with acid, or the sample is directly decomposed by acid, if the silicate is one of those amenable to this treatment. In the decomposition of the melt, variations may be made in the choice of acid and in its concentration. A number of authors prefer to decompose the melt with acid of high concentration [1,2], but others regard this point as unimportant [3,4,5]. Hydrochloric acid is most often recommended, but sometimes nitric acid, sulfuric acid, or perchloric acid is preferred.

2. Evaporation to dryness of the solution obtained and drying of the residue in order to achieve the maximum dehydration of the separated silicic acid and to convert it into the slightly-soluble form. Drying is carried out either by maintaining the residue in a dish on a boiling water-bath, the heating time not being precisely specified by the methods, or it is recommended that the residue should be dried in a thermostat at a temperature of 105-120° and higher.

Evidently, the nature of the salts present in the residue and their proportions, and also the nature of the dish, whether platinum or porcelain, in which the operation is carried out are not matters of indifference. Platinum is preferred because the transference of the separated silicic acid to the filter is more easily effected with a platinum dish than with a porcelain one; on the other hand, with a porcelain vessel a small increase in the weight of the silicic acid, due to corrosion of the vessel by acid, is unavoidable; it is generally considered that with porcelain vessels these two sources of error compensate one another, since they cause errors opposite in sign. In addition to this the conditions of drying on a boiling water bath with platinum and with porcelain vessels are not strictly comparable.

3. Treatment of the dried residue with concentrated acid in order to dissolve basic salts of iron, aluminum, titanium, and other metals, followed by extraction of the dry residue with water to bring the salts into solution. According to the existing procedures, the digestion of the dry residue with acids and the extraction of the salts may be carried out in different ways; both the quantity and the concenration of the acid may vary, as well as the time of digestion and the temperature at which the operation is carried out.

4. Filtration and washing of the residual insoluble silicic acid. The washing of the silicic acid is of essential importance for completeness of separation. There is no agreement as to how this operation should be carried out. It is recommended that the residue of separated silicic acid should be washed with water, or with acid solutions of different concentrations or even with ammonium nitrate solution; the recommended temperatures for the washing liquid also vary. It is not made sufficiently clear in the literature to what degree the silicic acid is reversibly dissolved in the washing liquid when the precipitate is being washed and what factors have a significant effect in this process.

5. Separation of silicic acid remaining in solution by a second evaporation of the filtrate and repetition of the operations described above.

6. Ignition of both silicic acid precipitates to constant weight, treatment of the silica with hydrofluoric

and sulfuric acids (as a check), evaporation of the acids, ignition and weighing of the non-volatile residue. This operation is generally carried out in the same way; the ignition temperature must be high.

7. Separation of silicic acid from the trioxides, its ignition to constant weight, and control treatment with hydrofluoric and sulfuric acids.

It is known that silicic acid is not completely separated by the two-stage evaporation of acid solutions. The silicic acid remaining in solution is brought down with the tri-hydroxides when ammonia is added to precipitate these. The separation of the silicic acid from the trioxides is the seventh, or last, of the analytical operations described above. This operation is not always carried out by analysts because it is generally considered that the two-stage evaporation of the solution results in almost complete separation of the silicic acid, the amount remaining in solution being small enough to be neglected. However, the results obtained by several workers show that the trioxide precipitate often contains significant quantities of silicic acid [6, 7]. The separation of silicic acid from the R_2O_3 precipitate is carried out either by dissolving the oxides in sulfuric acid or by fusing them with potassium pyrosulfate.

Thus, there is no uniform procedure for carrying out the "classical" method for the separation and gravimetric determination of silicic acid. Although the method has been repeatedly studied, there is no uniform procedure for carrying out the operations in the analytical literature or in the text-books on silicate analysis. And variants which differ still more widely are used in laboratories which carry out silicate analyses. The greater part of the work on the study of the separation of silicic acid by evaporating solutions is devoted to two operations of the method, namely, the dehydration of the residue obtained by evaporating the acid solution, and the washing of the separated silicic acid; these two operations are the object of special interest on the part of investigators.

In studying the dehydration conditions investigators have paid great attention to the temperature at which the residue of salts is dried, from the point of view of obtaining a complete separation of silicic acid and a residue of high purity. Investigators differ in their opinions as to what is the best drying temperature. In a text book on the analysis of minerals [3], it is recommended that the residues from the first and second evaporations should be dried entirely on a boiling water bath; this temperature is considered sufficient to convert the silicic acid into the difficultly soluble state.

The work of Gilbert [8] has also shown that dehydration of the dry salts in a thermostat at a temperature above 100° has no advantages over dehydration on a boiling water bath insofar as complete separation of silicic acid is concerned. However, a number of investigators recommend, on the basis of their own work, that the dehydration should be effected at a temperature of 105-120°, as they consider that a more complete separation of silicic acid is achieved by the use of such a temperature [9, 10, 11]. As a result of this work, Hillebrand and Lundel [4] and Kolthoff and Sandell [5] recommend that the residue from the second evaporation be dehydrated at 105-110°. Finally, several methods stipulate the still-higher dehydration temperature of 140° [12, 13, 14].

In most cases studies on the relation between dehydration temperature and completeness of separation of the silicic acid have been carried out on natural or on technical silicates, i.e., with silicic acid separated from solutions containing various salts. More attention has been devoted to the effect of dehydration temperature than to the effect of various salts on completeness of separation. The problem of contamination of the separated silicic acid by various impurities in relation to the dehydration temperature employed is the one which has been most studied.

Gilbert [8], in the course of analyses on fireproof materials and feldspars, studied the effect of dehydration temperature on the completeness of separation of silicic acid and on its purity when significant quantities of aluminum, calcium, and magnesium salts are present. According to his results, the presence of calcium or aluminum does not increase the amount of silicic acid which goes into solution even when the dehydration temperature is as high as 280°; but as a result of the formation of magnesium silicate which is decomposed by hydrochloric acid, the presence of magnesium causes an increase in the silicic acid solubility, even when the dehydration temperature is as low as 120°. On determining the purity of the silicic acid separated at the higher dehydration temperatures, the author found no calcium, but with the same dehydration conditions small amounts (tenths of a milligram) of magnesium were detected.

Jordis [15] studied the analysis of barium, strontium, and calcium silicates, which are decomposed by hydrochloric acid. His work showed that the separation of silicic acid is least complete in the analysis of calcium silicate, a more complete separation being achieved with barium and strontium silicates. However, as a criterion of completeness the author uses the sum of the percentages of SiO_2 and basic oxide, which is close to 100%. In addition, in the filtrate after separation of SiO_2 and basic oxide (BaO) the author found a residue amounting to 2% (instead of the calculated deficiency of 0.14%), which he attributed to "impurities". For this reason the author's results must be held in doubt.

Jordis and Ludewig[13] in studies on calcium, strontium and barium silicates, decomposed by acids, used special conditions for the separation of silicic acid from solution in order to show more clearly the relationship between its solubility and the presence of these cations. In the dehydration, they achieved a more complete removal of HCl by boiling the residue twice in succession with water and heating until the odor of HCl had completely disappeared. Under these conditions the solubility of the dehydrated silicic acid was greatly increased, and the effect showed a progressive increase, in the order barium to calcium. Under the same conditions, the presence of alkali salts caused a still greater increase in the silicic acid solubility.

Lenher and Troug [16] studied the effect of dehydration temperature on contamination of the separated silicic acid, the acid being separated from solutions containing salts of calcium, magnesium, and iron. The authors' results show that, in the presence of calcium the silica separated is only slightly contaminated with this metal, although a dehydration temperature of 150° was employed. This conclusion agrees with the results given by Hillebrand [17], who also found no calcium in the SiO_2 obtained in the analysis of various silicates. According to Lenher and Troug, when silicic acid is dehydrated in the presence of magnesium at temperatures higher than 115°, marked "contamination" of the residue with magnesium takes place. In the presence of iron, the silicic acid separated always contained significant quantities of this metal even in those cases where the dehydration temperature did not exceed 110°.

The amount of silicic acid which passes into solution when the precipitate is treated with solutions of varying composition depends to a large extent on the washing process. This problem has also been the subject of a number of investigations. The most complete study of the solubility of silicic acid in solutions of hydrochloric and sulfuric acid of varying concentration is that of Lenher and Merrill [18]. According to their results, the silicic acid solubility increases as the concentration of hydrochloric or sulfuric acid in the washing liquid decreases, maximum solubility being reached with pure water. It was also shown that the solubility increases with temperature. The numerical results given by these authors were obtained under conditions which ensured that equilibrium was attained (i.e., on saturated solutions of silicic acid). They showed that at a temperature of 25° the equilibrium state is reached in a few days, and at 90°, in a few hours.

The data obtained are of interest, but it is utterly impossible to draw analytically useful conclusions from them, because the conditions under which the solution acts on the silicic acid in the analytical process are entirely different from those under which the authors conducted their experiments. However, the characteristics of the dissolution process, i.e., dependence of silicic acid solubility on the concentration of mineral acid and the effect of temperature on solubility, are obviously valid under analytical conditions.

Lenher and Troug [16] showed that when dehydrated silicic acid was treated with concentrated, with 20%, and with 10% hydrochloric acid, the maximum loss occurred with the 10% acid; treatment with 20% acid gave results close to those obtained with the concnetrated acid. The same authors showed that when dehydrated silicic acid was washed with solutions of HCl, NaCl, and NH_4Cl, and also with water, the greatest loss was found with NH_4Cl solution, a smaller loss with NaCl solution, and the minimum loss with water. Bucherer and Meier [9] studied the effect of washing silicic acid, which had previously been washed free of chloride ions, with hydrochloric acid of different concentrations; they showed that the minimum loss occurred with 10% HCl, a greater loss with 15%, and the maximum loss with 20% HCl. These results are not in accord with the data of investigators already cited.

Hawley [12], studying the loss of dehydrated silicic acid by dissolution, concluded that its solubility is at a maximum in 15-25% solutions of hydrochloric acid; with higher or lower concentrations of hydrochloric acid the solubility decreases (the author gives concentrations in volume percentages; the calculated weight percentages corresponding to these are 6.5-11%). According to the author, the solubility in pure water is extremely low, but it is greatly increased in the presence of sodium chloride. All the authors cited determined the qua quantity of dehydrated silicic acid passing into solution by evaporating the wash-water, dehydrating the dry residue, and treating it so as to remove the silicic acid by filtration, i.e., in a manner which, in our opinion, makes complete separation impossible.

In view of the contradictory results obtained by various authors cited above, we carried out an experimental study in order to elucidate the effect of dehydration temperature and the effect of the nature of washing solutions on the completeness of separation of silicic acid from solutions used in its analytical determination.

EXPERIMENTAL

A series of dehydration experiments was carried out at different temperatures in order to find the effect of temperature and of duration of dehydration on the completeness of separation of silicic acid. A sample of amorphous chemically pure silica, which had been previously heated to constant weight, was used as starting material in all the experiments. Its purity was first checked by treatment with hydrofluoric and sulfuric acids. The non-volatile residue obtained by calcining the silica amounted to 0.1%. The content of non-volatile impurities (0.1%) was taken into account in calculating the sample weights for individual experiments. The sample weight amounted to 0.3-0.4 g. The sample was fused with a six-fold quantity of Na_2CO_3, the melt extracted in a platinum dish with water and decomposed with concentrated hydrochloric acid. The acid solution was evaporated to dryness and the dehydration carried out at different temperatures. The dehydrated gel was treated with 5 ml of concentrated hydrochloric acid for 5 minutes, and after dilution to about 50 ml with water, the solution was maintained on a boiling water bath for 10-15 minutes to dissolve salts (NaCl). The separated silicic acid was removed by filtration and washed with hot dilute hydrochloric acid (in some experiments) or with water. The filtrate was evaporated a second time and after dehydration of the dry residue under the same conditions a second silicic acid precipitate was obtained.

The silicic acid precipitate from the second evaporation was washed either with dilute hydrochloric acid (1: 99) or water (in those cases in which hot water was used to wash the main precipitate from the first evaporation). Both silica precipitates were ignited to constant weight. The ignited silica was checked for purity by treatment with mixed acids ($HF + H_2SO_4$).

The results obtained by dehydrating silicic acid at 100° are given in Table 1.

TABLE 1

Expt. No.	Separation conditions			SiO_2 found as percent of quantity taken
	Dehydration		Composition of washing solutions*	
	Temperature (°C)	Hours heated		
1	On boiling water bath	3	Hot water	99.13
2	"	3	"	99.43
3	"	3	"	99.58
4	"	1	"	99.77
5	"	1	"	99.69
6	"	1	"	99.62
7	"	1	Hot solution of HCl (5: 95)	99.32
8	"	1	"	99.73
9	"	1	"	99.20
10	"	1	"	99.15
11	"	1	"	99.51
12	"	1	"	99.12
13	In thermostat at 98-100°	1	"	99.37
14	"	1	"	99.37
15	"	1	"	99.51
16	"	1	"	99.22
17	"	1	"	99.21
18	"	1	"	99.20
19	"	1	"	99.60
20	"	1	"	99.67

* This solution was used for washing the main silicic acid mass (first separation). The silicic acid obtained in the second separation was washed with dilute hydrochloric acid solution (1: 99).

TABLE 2

Expt. No.	Separation conditions		SiO_2 found as percent of quantity taken
	Dehydration temperature (°C)	Composition of washing solution	
1	108-110	Hot solution of HCl (5: 95)	99.41
2	108-110	"	99.79
3	108-110	"	99.80
4	108-110	"	99.71
5	108-110	"	99.79
6	108-110	"	99.43
7	108-110	"	99.68
8	108-110	"	99.62
9	108-110	"	99.51
10	108-110	"	99.55
11	108-110	"	99.52
12	108-110	"	99.65
13	108-110	"	99.60
14	108-110	"	99.62
15	108-110	"	99.76*
16	108-110	"	99.73*
17	114-120	"	99.86
18	114-120	"	99.27
19	114-120	"	99.52
20	114-120	"	99.52
21	114-120	"	99.77

* Melt decomposed by HCl (1: 1)

As will be seen from these figures, whether dehydration is carried out for one hour or for three hours makes no material difference in the quantity of silicic acid separated. The quantity of silicic acid separated amounts on the average to 99.43% of SiO_2 based on the amount of SiO_2 taken (mean of 20 determinations).

The deviations between the individual determinations lie within the limits 99.12-99.77%. When the silicic acid obtained under identical dehydration conditions was washed with different washing solutions — dilute hydrochloric acid and water — there was no material difference in the SiO_2 results obtained.

In the next series of experiments the dehydration was carried out at higher temperatures, namely 108-110° and 114-120°, for one hour. The results obtained are given in Table 2.

When the dehydration temperature is raised to 110° the quantity of silicic acid separated is slightly greater, and the deviation between individual SiO_2 determinations less, than that found when the dehydration is carried out at a temperature of about 100°. The mean value for the SiO_2 found is 99.61%, and the deviations between duplicate experiments lie within the limits 99.41 and 99.80%.

In experiments 15 and 16, the melt was decomposed with HCl (1: 1) and good agreement was obtained between duplicates (99.73-99.76). The higher dehydration temperature of 114-120° does not, it appears, increase the quantity of silicic acid separated — the mean SiO_2 content from five determinations is 99.58%, and deviations between duplicates lie within a range of 0.5%.

In order to find the effect of the composition of the solution on completeness of separation, we carried out experiments on the separation of silicic acid from hydrochloric acid solutions which contained considerable amounts of sodium chloride, the chlorides of calcium, magnesium, titanium, and aluminum being also present. The dehydration was effected on a boiling water bath for one hour. In each experiment a weighed sample of the appropriate oxide was added to the sample (0.3-0.4 g) of chemically pure SiO_2, previously ignited to constant weight. The mixture of oxides was fused with sodium carbonate. The melt was decomposed with HCl (1: 1). The results are given in Table 3.

TABLE 3

Expt. No.	Weight, in g					SiO_2 found as percent of quantity taken		
	CaO	MgO	TiO_2	Al_2O_3	$SiO_2 : RO_n$ (weight)	Separation 1	Separation 2	Total
1	0.086	–	–	–	4.3	99.08	0.92	100.00
2	0.086	–	–	–	3.7	99.21	0.70	99.91
3	0.170	–	–	–	2.1	98.97	1.03	100.00
4	0.170	–	–	–	2.1	99.32	0.68	100.00
5	–	0.055	–	–	5.6	98.41	0.70	99.11
6	–	0.055	–	–	5.6	98.36	0.96	99.32
7	–	0.110	–	–	3.1	98.85	0.65	99.50
8	–	0.110	–	–	2.9	98.53	1.12	99.65
9	–	–	0.025	–	14.7	99.13	0.60	99.73
10	–	–	0.025	–	14.0	99.26	0.51	99.77
11	–	–	0.031	–	11.4	98.70	0.96	99.66
12	–	–	0.031	–	12.4	98.54	1.15	99.69
13	–	–	0.015	–	20.4	98.79	0.98	99.77
14	–	–	–	0.160	2.4	–	–	99.90
15	–	–	–	0.160	2.0	–	–	100.09

As these results show, the presence of calcium or aluminum promotes more complete separation of SiO_2. This agrees with the work of Gilbert, but is not in accord with the results obtained by Jordis and by Jordis and Ludewig. It should be mentioned that Jordis carried out his investigations on calcium silicates, which are decomposed by acids, in the presence of alkali salts. It is possible that under these conditions the silicic acid is not sufficiently dehydrated. We know that in the decomposition of carbonate rocks the soluble silicic acid obtained is difficult to dehydrate by evaporating acid solutions in the presence of considerable quantities of calcium chloride. Further studies by these authors (Jordis and Ludewig) are not comparable with our results because of the material changes which they made in the analytical conditions.

Our results show that the presence of magnesium (Expts. 5-8), slightly reduced the amount of silicic acid separated, though the dehydration temperature was not above 100°. In these experiments the non-volatile residue obtained after treatment of the ignited silica contained magnesium in amounts corresponding to 0.4-0.2 mg of MgO. The presence of titanium (Expts. 9-13), apart from causing significant contamination, had no marked influence on the completeness of separation.

Investigation of the effect of dehydration temperature on completeness of separation of the silicic acid from solutions showed that variations in temperature (above 100°) had comparatively little effect on the quantitative separation of SiO_2. Nevertheless, when the silicic acid was dehydrated at a temperature close to 100°, slightly lower average values for SiO_2 were obtained. It should also be mentioned that in our experiments, platinum vessels were used, and under these conditions when the dry residue is heated on a boiling water bath the dehydration temperature is close to 100°. When porcelain vessels are used under the same conditions, the dehydration will take place at a lower temperature, and it is possible that still lower SiO_2 values will be obtained. When porcelain vessels are used, it is therefore advisable to carry out the dehydration in a thermostat at 108-110°. A higher temperature (118-120) will not increase the quantity of silicic acid separated, but if magnesium salts are present, it will increase the loss of silicic acid when the dry residue is later treated with acid solutions.

In order to determine to what extent the separated silicic acid passed into solution, we carried out experiments in which it was washed with hot water and with dilute hydrochloric acid solutions. In these experiments we made separate determinations of the silicic acid separated by dehydration, the silicic acid in the main filtrate, and the silicic acid in the washing-liquids, which were collected separately. There are two possible sources of the silicic acid in the main filtrate: it may be due either to incomplete conversion of silicic acid to the difficultly-soluble form in the course of dehydration, or to reversible solution of this form when the dry residue is treated with an acid solution containing considerable quantities of sodium chloride. There are many references in the literature to the enhanced solubility of silicic acid in the presence of alkali metal chlorides, but at present it is not possible to say which of these causes is of the greatest significance.

The amount of silicic acid in the main filtrate and in the washing liquids, the volume of which was 300 ml in all the experiments, was determined by precipitating the silicic acid with aluminum hydroxide. We used artificial solutions to work out the method of separating silicic acid by coprecipitation. The amount of alumina required for the quantitative separation of silicic acid from solution by coprecipitation with aluminum hydroxide was determined from experimental data.

In all the experiments carried out the conditions used for the dehydration and digestion of the silicic acid were identical. The weighed sample of calcined SiO_2 (chemically pure) was fused with 2 g of Na_2CO_3. The melt was decomposed on a platinum dish with 20 ml of HCl (1: 1), and the solution was evaporated to dryness on a boiling water bath. The dry residue was ground with a glass pestle and dehydrated for an hour at a temperature of 105-110°. The cooled dry residue was moistened with 5 ml of concentrated hydrochloric acid and the dish was allowed to stand covered with a watch glass for 2-3 minutes, after which 45 ml of water was added and the covered dish placed on a water bath for 10 minutes to dissolve the salts. The silicic acid separated was removed by filtration. The main filtrates were collected separately from the washing liquids.

TABLE 4

Expt. No.	SiO_2 found, as % of quantity taken			
	Separated by dehydration	In main filtrate	In washing liquids	Total
1	98.54	0.63	0.89	100.06
2	98.59	0.77	0.69	100.03
3	98.97	0.45	0.53	99.95
4	98.53	0.55	0.80	99.88
5	98.56	0.58	0.77	99.91
6	98.01	0.95	1.00	99.96
7	97.43	0.96	1.48	99.92
8	98.04	0.77	1.34	100.15

Note. In Experiments 1-3 the separated silicic acid was washed with hot dilute hydrochloric acid (5: 95); in Experiments 4-6, with hot water, and in Experiments 7-8 with hot 10% HCl solution.

In Experiments 1-3 the separated silicic acid was washed with hot dilute hydrochloric acid (5: 95), in Experiments 4-6 with hot water, and in Experiments 7-8 with hot 10% HCl solution. In all the experiments the volume of the washing liquid was the same, 300 ml. The results obtained are given in Table 4.

The results obtained show that:

1. The total amount of SiO_2 found in all the experiments is close to 100%, from which it follows that there were no notable silicic acid losses.

2. The quantity of silicic acid in the main filtrate obtained after separating the bulk of the silicic acid varied within wide limits in replicate experiments: the limits were 0.45 to 0.96% (based on the amount taken). This suggests that, in spite of identical dehydration conditions and relatively close absolute weights of the silicic acid starting material (0.33-0.41 g), the amount remaining in solution may vary, i.e., completeness of precipitation is determined by other, unknown factors. It seems to us that an important factor here is the degree of polymerization of the silicic acid in the operations preceding dehydration.

3. When hot dilute hydrochloric acid (5: 95) was used as the washing liquid, the amount of silicic acid

dissolved in it was 0.53 to 0.89%. With hot water a somewhat larger amount was lost (0.77-1.00%). With hot 10% HCl solution a still greater loss was observed (1.48-1.34%). For this reason, hot, very dilute solution of hydrochloric acid (5: 95) is recommended for washing the precipitate of silicic acid separated from hydrochloric acid solutions.

SUMMARY

1. A study was carried out on the effect of dehydration conditions (time and temperature of dehydration, presence of salts) and of washing processes on the completeness of separation of silicic acid from solutions.

2. It has been shown that the completeness of separation by dehydration depends not only on the choice of conditions of dehydration, washing, and other analytical factors usually regarded as significant, but also on some unknown factors; it is suggested that completeness of separation of silicic acid depends on the degree of polymerization of the silicic acid produced in the treatment which precedes dehydration of the salts.

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STUDY OF THE "COMPOSITION – HEAT-STRENGTH" DIAGRAM FOR ALLOYS OF THE QUATERNARY SYSTEM IRON – CHROMIUM – NICKEL – MANGANESE

I. I. Kornilov and K. A. Osipov

In recent years [1,2] systematic studies have been carried out by the centrifugal method on the strength of metallic alloys at high temperatures. Up to the present, studies by this method have included alloys of a number of binary systems, Al–Mg, Mg–Cd, Ni–Cr [3,4], and alloys of the ternary system, Fe–Cr–Ni [1], corresponding to continuous or limited solid solutions of these systems. In these studies some relationships have been established between phase nature and structure and the character of the "composition – heat-strength" diagrams

There are no references in the literature to systematic studies of the "composition – heat-strength" diagrams for alloys of the quaternary system iron – chromium – nickel – manganese. The authors have studied the diagram of this system over the past few years.

EXPERIMENTAL

In the present paper experimental results obtained in a study of the electrical resistance, hardness at room temperature, and heat-strength at 800° of alloys of one section of this quaternary system are given. The basic section used was that of the ternary system iron – chromium – nickel, passing from the chromium corner to the binary system iron – nickel with iron and nickel in constant (1 : 1) proportions; its apex corresponds to the apex of the tetrahedron representing a manganese content of 100%.

Fig. 1 represents part of this section for a temperature of 800°. The boundary of the γ solid solution marked here on the ternary iron – chromium – nickel side was drawn from data given in the literature [5]. Data obtained from experimental studies of microstructure, hardness, and specific electrical resistance on alloys tempered at 800° were used in constructing the boundaries at the ternary iron – nickel – manganese side, as well as at other parts of the quaternary system. After casting, all of the alloys were subjected to homogenizing annealing treatment for 48 hours at 1100°, slow cooling in the furnace to 800°, and tempering at that temperature.

Not all the two-phase and three-phase regions adjacent to the solid solution were studied in detail, and for this reason some of them are denoted on Fig. 1 by dotted lines. The alloys situated close to the boundary of the solid solution were chemically analyzed. The analyses showed only insignificant deviations in composition from the figures obtained by calculation. Most of the alloys were therefore not subjected to chemical analysis.

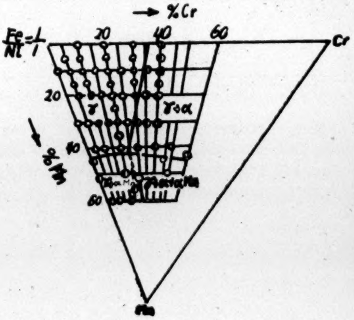

Fig. 1. Isothermal section of the quaternary system at 800°: o – one phase; ● – two phases; ● – three phases.

Fig. 2 shows the relationship between specific resistance and composition for alloys of this section tempered at 800°. Here each curve represents alloys of constant manganese content, the proportions of the other components varying. The change in the course of a curve corresponds to a change in the phase composition of the alloys – from the single-phase region of the γ solid solution to the two-phase region, γ + α, and this was confirmed by microanalysis. It is noteworthy that the specific resistance of the γ solid solution remains almost constant when its chromium content varies; and an increased manganese content has little effect here. Transition from the γ solid solution to the two-phase region, γ + α, is accompanied by a significant increase in hardness.

The diagram composition – heat-strength for the alloys of the section considered was studied by measuring the bending deflection of samples under the action of centrifugal force [1]. Cast samples, 80 mm long and 3.85 mm in diameter, were first annealed for 48 hours at 1100° and then subjected to bending for definite periods of time (6, 12, and 16 hours) at 800°; after each period, the bending deflection was measured. The initial deformation stress chosen was 2.78 kg/mm².

Curves showing the dependence of bending deflection on the chemical composition of the alloys are given in Figs. 4, 5, and 6. These show that for a given manganese content the bending moment of alloys from the region of γ solid solution sharply decreases when the chromium content of the alloys increases. Transition from the region of the γ solid solution to the two-phase γ + α region is accompanied in all cases by a significant increase in the bending deflection. Consequently, for this quaternary system, as for the ternary system, Fe – Ni – Cr [1], it is confirmed that heterogenization of the γ solid solution by the second solid solution, α, leads to a reduction in the heat-stability of the alloys, or the resistance of the alloys to plastic deformation at high temperatures. Here it should be noted that there is no direct relationship between changes in strength at room temperature (as shown by hardness) of alloys with heterogeneous and homogeneous structures in their composition and the heat-strength of the same alloys. On the contrary, heterogeneous alloys possessing a high degree of hardness at room temperature show the lowest heat-strengths at 800° (see Figs. 3, 4, 5, and 6).

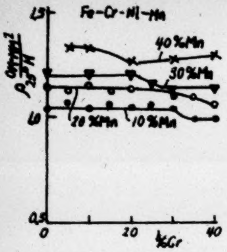

Fig. 2. Specific electrical resistance of quaternary alloys tempered at 800° in relation to composition.

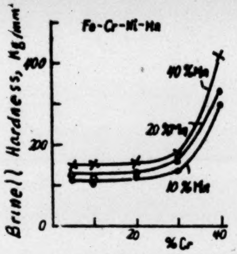

Fig. 3. Hardness of quaternary alloys tempered at 800° in relation to composition: ● – 10% manganese; o – 20% manganese; x – 40% manganese.

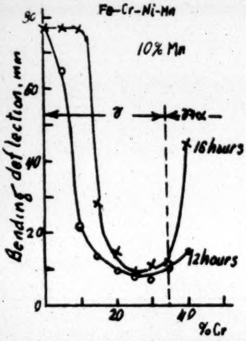

Fig. 4. Relation between bending deflection of quaternary alloys at 800° and chromium content (10% manganese).

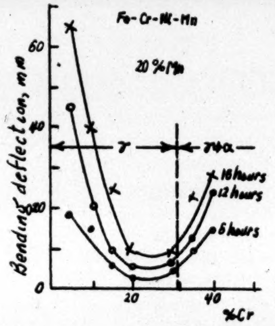

Fig. 5. Relation between bending deflection of quaternary alloys at 800° and chromium content (20% manganese.

It is also of interest that, for the section of the iron – chromium – nickel – manganese quaternary system considered here, an increase in the bending deflection of the alloys becomes evident long before the composition enters the two-phase region. The increase is noticeable even before the composition reaches the boundary of the solubility limit of the components in the γ solid solution. Examination of the alloys, before application of the bending forces, by microanalysis and by measurement of specific electrical resistance and hardness, failed to reveal the presence of a two-phase system in any of those which had a composition in the γ solid solution region close to its boundary, and which showed a decrease in the bending deflection before this boundary is crossed. There is reason to believe that the increased plastic flow of the solid solution in this system, as shown by alloys of composition close to the solubility limit, is connected with the degree of tempering of the original solid solution and with other factors.

Our experiments show that manganese does not reduce the plastic deformation resistance of alloys having compositions corresponding to the solid solution of the iron – chromium – nickel – manganese quaternary system. On the contrary, an increase in manganese content leads to an increase in this resistance, though the effect is slight. This can be seen from Fig. 7, which shows the relationship between the bending deflection of alloys of the section under discussion and the manganese content, the chromium content being kept constant at 20%. The experimental points were obtained by testing for 11 hours at 800° and 4 hours at 900°. From the results given

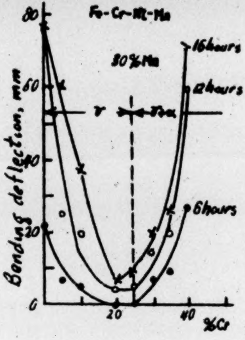

Fig. 6. Relation between bending deflection of quaternary alloys at 800° and chromium content (30% manganese).

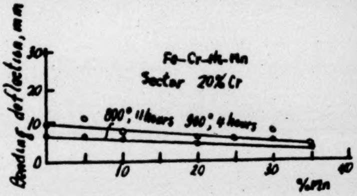

Fig. 7. Effect of manganese on the bending deflection at 800° on the quaternary γ solid solution.

here it may be concluded that for some alloys for use at high temperatures the nickel content can be reduced at the expense of the manganese. It should, however, be borne in mind that an increase in the manganese content leads to a reduction in the heat stability of the alloy. For this reason, when manganese is used in the preparation of alloys, other elements which increase the heat stability should also be included. As will be evident from the literature, other authors, studying manganese alloys by different methods, have arrived at similar conclusions.

SUMMARY

1. The results are given of a study of alloys of one section of the iron – chromium – nickel – manganese quaternary system, in which measurements were made of the electrical resistance and the hardness at room temperature, and of the heat-strength at 800°.

2. The composition – heat-strength diagram for the alloys of this system shows that in the region of the quaternary γ solid solution the heat-strength markedly increases with the chromium content of the solid solution. An increase in the chromium content above the saturation limit or into the region of the γ + α phases leads to a sharp reduction in the deformation resistance of the alloys at 800°.

3. The hardness of the heterogeneous alloys (γ + α phases) at room temperature sharply increases with an increase in the chromium content, but the heat-strength of the alloys in the same heterogeneous region is sharply reduced.

4. An increase in the manganese content of the quaternary solid solutions results in a slight increase in the heat-strength of these alloys.

From the experimental results obtained, it can be stated that in many alloys which have as their basis the system iron – chromium – nickel, a considerable quantity of the nickel can be replaced by manganese without materially altering the plastic deformation resistance. But this replacement of nickel by manganese should always be accompanied by the inclusion of supplementary alloying components which are capable of increasing the heat stability of the alloys.

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THERMOCHEMICAL INVESTIGATIONS OF SOLUTIONS

COMMUNICATION 5. VAPOR PRESSURE AND COMPOSITION OF THE BINARY SYSTEM $CH_3CHO + H_2O$

A. A. Dobrinskaya, V. G. Markovich, and M. B. Neiman

In the course of our work on the cold-flame oxidation of hydrocarbons [1-3], we found it necessary to distil aqueous solutions of various aldehydes, including acetaldehyde. It was found that there is practically no data in the literature on the vapor pressure and composition of acetaldehyde solutions. However, this problem is of theoretical as well as practical interest, since it is known that acetaldehyde tends to form hydrates, and for this reason its aqueous solutions should show large deviations from the laws of ideal solutions.

The vapor pressure and composition of aqueous solutions of acetaldehyde were determined by Pascal and his coworkers [4], by Kovalev [5], and by Bushmakin and Kuchinskaya [6]. The work of Pascal was carried out over 30 years ago by the method of distilling mixtures of acetic acid, acetaldehyde and water; it was intended to provide data required by chemical factories engaged in the production of synthetic acetic acid. Bushmakin and Kuchinskaya give total vapor pressures for dilute solutions only.

Tentative values for the partial vapor pressure of acetaldehyde were obtained by these authors on the assumption that the partial vapor pressure of the water could be calculated from Raoult's law. Such an assumption is, or course, open to criticism. Because of the faulty methods used by Kovalev in that part of his work dealing with the determination of vapor tension, his results cannot be regarded as trustworthy.

In view of this situation, we undertook the work of determining the vapor pressure and composition of aqueous acetaldehyde solutions over a wide range of concentrations and in the temperature interval 0 to 25°.

EXPERIMENTAL

1. Experimental methods

The acetaldehyde used was prepared from commercial acetaldehyde through paraldehyde, the paraldehyde being purified by double distillation. The acetaldehyde was obtained by depolymerizing the paraldehyde with the aid of a small quantity of concentrated sulfuric acid, and it was then twice distilled in a nitrogen atmosphere. The product has a boiling point of 19.8° at 760 mm; its vapor pressure values at different temperatures agreed closely with the values obtained by Gilmour [7].

The acetaldehyde content of the solutions was determined by the hydroxylamine method. As will be seen from the results of several analyses given in Table 1, acetaldehyde can be determined by this method with an error not exceeding 1-1.5%. The total vapor pressure of the acetaldehyde solutions was determined by the static method already described by one of the present authors, [8].

TABLE 1

Test of Hydroxylamine Method for Accuracy

Concentration of CH_3CHO, in weight %					CH_3CHO found, as% of taken
Taken	Found				
	I	II	III	Mean	
2.86	2.84	2.84	2.81	2.83	98.9
4.85	4.89	4.85	4.87	4.87	100.4
8.20	8.08	8.07	8.09	8.08	98.5
20.5	20.30	20.36	20.39	20.35	99.2

A vacuum apparatus, part of which is shown diagrammatically in Fig. 1, was set up for the preparation of air-free acetaldehyde solutions. The vessel 1, containing acetaldehyde, was connected to the vacuum line by means of a rubber tubing. The acetaldehyde was cooled in liquid air and the apparatus was evacuated through taps 2 and 5, with tap 7 open. The Dewar vessel of liquid air was then placed under vessel 3, tap 5 was closed, and the acetaldehyde was distilled into 3. The air which was given off in this process, and whose pressure could be measured by the manometer 8, was pumped out, tap 2 being closed and tap 5 open. Then tap 5 was closed, the Dewar vessel brought under 4, and the acetaldehyde was distilled 3 into 4. The air given off was again pumped out. The process of distilling the acetaldehyde from 3 into 4 and back again, the air being pumped out after each operation, was repeated until air was completely removed from the apparatus.

Taps 5 and 7 were next closed and the solidified aldehyde was retained in vessel 3 or 4. Vessel 11, containing distilled water, was then attached to the line by means of rubber tubing. The water was frozen, and the air pumped out through taps 12 and 10. Tap 10 was next closed, and the Dewar vessel of liquid air brought under 9, into which the water was distilled. The air liberated from solution was pumped out. Air was completely removed from the system by distilling the water backward and forward between vessels 11 and 9, the air being pumped out after each operation. The trap 6, cooled with liquid air, prevented both water and acetaldehyde from reaching the pump during all these operations.

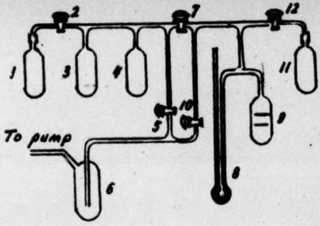

Fig. 1. Diagram of apparatus for the preparation of air-free solutions of acetaldehyde in water.

Two marks were made on vessel 9, the upper one corresponding to the total volume of solution to be prepared, and the lower one to the volume of the water component of this solution. A sufficient quantity of water was distilled into vessel 9 to bring its level a little above the mark. Tap 12 was then closed, and the excess water together with traces of air was pumped out through tap 10. Tap 10 was closed, and the water in 9 frozen. Tap 7 was opened and the acetaldehyde was carefully distilled into 9 until the level of the solution reached the upper mark. Tap 7 was then closed, and the vessel 9, together with the manometer, was sealed off from the apparatus at the neck. The solution was mixed by shaking the vessel. The vessel was then immersed in a thermostat, the temperature of which was maintained constant to within 0.01°. In order to avoid condensation of the vapors, the part of the apparatus which protruded from the thermostat was heated by means of an electric current. The vapor pressure of the solution was determined at 0, 12.04, and 24.77°. After the measurements had been made, the solution was frozen, the vessel opened, and the acetaldehyde content of the solution determined by the hydroxylamine method.

The partial vapor pressure of acetaldehyde was determined by a dyanmic method which has often been employed by Vrevsky [9,10], by Schawa and Butler [11], as well as by other workers. The apparatus is shown diagramatically in Fig. 2. The method of operation of this apparatus is briefly described below.

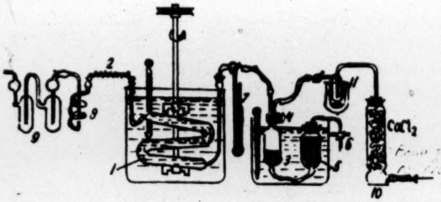

Fig. 2. Diagram of apparatus for the determination of the partial vapor pressure of acetaldehyde by the dynamic method.

The mercury gas reservoir 3, was filled to the mark with dry nitrogen, passed through the the tower 10 and the trap 11; its pressure was read on the manometer 7, and the temperature was also taken; tap 4 was then closed and the levelling vessel 5 raised. The bubbler 1 was filled with cooled acetaldehyde solution by means of a funnel connected to the inlet tube with a ground joint. The exit tube openings of the bubbler were closed with stoppers. The bubbler was placed in a thermostat heated a little above the required temperature and connected to the manometer, the three-way tap being in the closed position. The heater of the exit tube 2 was switched on. The trap 8, closed with stoppers, was weighed on an analytical balance. One end of it was then connected to the sulfuric-acid bubble-gage 9, after which it was immersed in liquid air contained in a Dewar flask. When the pressure in the trap had reached atmospheric, the gage was connected to it at the return end. When the thermostat had reached the required temperature, the exit tube of the bubbler was connected with the trap; the tap 4 was carefully opened and the bubbling of nitrogen commenced at the rate of 15-20 bubbles per 10 seconds, which corresponds to ~500 ml per hour. The time of commencement of the experiment was noted from here. In some experiments, carried out to check the nitrogen absorption, the higher flow rate of about 500 ml per hour was employed. A constant rate of flow was maintained by gradually raising the levelling vessel 5 and checking on the bubble-gage. When all the nitrogen from the gas reservoir had passed through, tap 4 was closed, the trap was cut off from the bubbler, the exit tube of which was stoppered. The time of ending the experiment was noted here. During the course of the experiment, records were kept of the temperature of both thermostats, and of the pressure and rate of flow of the gas. At the end of the experiment, the trap was removed from the Dewar vessel, and kept with one exit tube open until the contents began to melt so as to equalize the pressure; it was then completely stoppered to prevent acetaldehyde losses. When the trap had reached room temperature it was weighed, after which its contents were transferred to a volumetric flask; the solution was made up to the mark and samples analyzed.

The volume of acetaldehyde vapor was calculated from the formula

$$V_{CH_3CHO} = \frac{22400 \cdot T \cdot 760 \cdot x}{273 \cdot p \cdot 44}, \qquad (1)$$

where T is the absolute temperature, $\underline{x}$ is the weight of acetaldehyde collected, and $\underline{p}$ is the pressure at which the experiment is carried out. The water vapor volume, V_{H_2O}, was calculated from a similar formula; the nitrogen volume V_{N_2}, was easily calculated from the volume of the mercury gas reservoir (447.7 ml) and the temperature and pressure of the nitrogen. The partial vapor pressure of acetaldehyde was calculated from the formula:

$$p_{CH_3CHO} = \frac{pV_{CH_3CHO}}{V_{N_2} + V_{CH_3CHO} + V_{H_2O}}. \qquad (2)$$

2. Experimental results

First we determined the total vapor pressures of acetaldehyde solutions and calculated the partial vapor pressures of acetaldehyde by means of Duhem's formula [12]. In order to check the validity of these calculated values, we made experimental determinations of the partial vapor pressure of acetaldehyde on a number of solutions.

Determination of the vapor pressure of the binary system $CH_3CHO + H_2O$. The results of our experimental determinations of the total vapor pressures of aqueous acetaldehyde solutions by the static method are given in Table 2.

The values we obtained for the vapor pressure of pure acetaldehyde agree to within 3-5 mm with those given by Gilmour [7] and by Roth [13].

Our results may be expressed by the formula

$$\log p = 7.821 - \frac{6000}{2.3\ RT}. \qquad (3)$$

from which it follows that the latent heat of vaporization of acetaldehyde in the temperature range 0-25° is equal to 6000 cal/mole. This value is in good agreement with the latent heat values found by Roth [13] (6020 cal/mole), and by Berthelot [14] (6000 cal/mole). In calculating the partial vapor pressures by Duhem's formula we attempted to make use of the method of Margules [15]. However, the use of this method with exponential terms containing only second and third powers of $\underline{x}$ gave unsatisfactory results. We therefore used the method of successive approximations proposed by Bose [16]. Using this method, we derived values for the partial vapor pressures of acetaldehyde and water from their sum

TABLE 2

Total Vapor Pressures of Aqueous Acetaldehyde Solutions

Quantity of acetaldehyde in solution		Pressure in mm Hg at temperature in °C		
Weight %	Mol. %	24.77	12.04	0.0
11.4	5.0	189.5	89	40
27.6	13.4	436	219	90
36.2	18.9	564	312	139
50.2	29.3	672	383	191.5
76.7	57.4	769	470	277
81.5	64.3	789	483	282
86.6	72.7	791	488	292
96.0	90.6	841	524	315
100.0	100.0	761*	562	346.5

* This determination was carried out at 19.8°.

$$p_{CH_3CHO} + p_{H_2O} = p \qquad (4)$$

and the relationship

$$\frac{p_{CH_3CHO}}{p_{H_2O}} = - \frac{x}{1-x} \frac{\frac{dp_{CH_3CHO}}{dx}}{\frac{dp_{H_2O}}{dy}} \qquad (5)$$

The latter relationship follows from Duhem's formula. Calculated partial vapor pressures of acetaldehyde for a number of solutions are given in Table 3. Total and partial vapor pressure curves of the solutions are shown in Figs. 3, 4, and 5. As will be seen from the curves, the vapor pressure of acetaldehyde solutions at all the temperatures studied have higher values than would be found if the solutions were ideal. The vapor pressure curves show no extreme values; therefore by Konovalov's law [17] aqueous solutions of acetaldehyde do not form azeotropes.

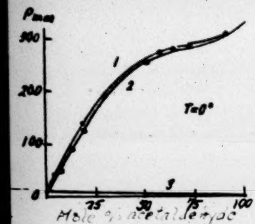

Fig. 3. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 0°: 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

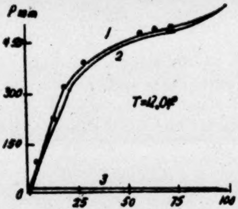

Fig. 4. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 12.04°. 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

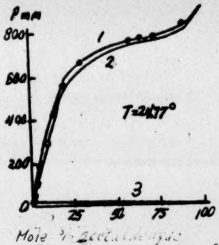

Fig. 5. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 24.77°; 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

Determination of the partial vapor pressures of acetaldehyde. Using the dynamic method, we determined the partial vapor pressures of acetaldehyde at 0 and at 24.77 The results of the experiments at 24 77 are given in Table 4.

As will be seen from a comparison of columns 3 and 4 in Table 4, where experimental results obtained in duplicate experiments on solutions containing 2 mole % CH_3CHO are given, good agreement is obtained in duplicate experiments. We carried out similar experiments at 0° on solutions containing 7.6, 13.0, 18.3, and 50.8 mole % of acetaldehyde. The results obtained are given in Table 5.

The difference between the results of duplicate experiments rarely exceeds 2%, even when concentrated acetaldehyde solutions having partial pressures as high as 350 mm are used.

Our experimental values for the partial vapor pressure of acetaldehyde are in good agreement with the corresponding values calculated from total vapor pressures by the Bose method. This is evident from an examination of Figures 3 and 5, where the experimental values denoted by circles closely follow the full line, which is drawn through the points obtained from the calculated values.

TABLE 3

Partial Vapor Pressures of Acetaldehyde Calculated by the Method of Bose

Quantity of acetaldehyde, mol. %	Pressure in mm Hg at temperature in °C		
	24.77	12.04	0.00
10	315	159	68
20	558	293	134
30	655	379	192
40	702	426	236
50	734	454	263
60	755	470	276
70	773	477	284
80	792	490	297
90	827	510	312

TABLE 4

Partial Vapor Pressure of Aqueous Acetaldehyde Solutions at 24.77 °C.

Concentration of acetaldehyde in solution	weight % / mole %	2.6 - / 1.05	4.85 / 2.0	4.85 / 2.0	8.2 / 2.5	20.4 / 9.50
Experiment No.		2	3	4	6	8
Nitrogen passed, in ml		457.8	462.5	459.3	457.3	461.1
Total weight of condensate, in g		0.0662	0.1018	0.1022	0.1763	0.6473
Weight of acetaldehyde, by analysis, in g		0.0430	0.0817	0.0814	0.1530	0.6180
Weight of water, by difference, in g		0.0232	0.0201	0.0207	0.0233	0.0293
Volume of acetaldehyde vapor, in ml		23.5	45.1	45.0	83.6	337.5
Total volume of nitrogen and vapors, in ml		512.3	534.7	532.2	572.0	837.7
Pressure, in mm		772.5	766.0	766.2	773.5	774.7
Acetaldehyde vapor pressure, in mm		35.5	64.6	64.8	113.1	312.0

TABLE 5

Partial Vapor Pressure of Acetaldehyde over Its Aqueous Solutions at 0°

Quantity of CH_3CHO		Pressure, in mm Hg		
Weight %	Mole %	Expt. 1	Expt. 2	Expt. 3
33.6	7.6	55.2	54.0	54.6
50.3	13.0	90.2	90.8	90.5
63.1	18.3	129.1	129.0	129.1
71.5	50.8	353.3	348.7	351.0

DISCUSSION OF RESULTS

Our values for the vapor pressure and composition of aqueous acetaldehyde solutions may be used to calculate the approximate heats of formation of the solutions. Indeed, as Kirchhoff [18] has shown, the partial vapor pressure of one component of a solution increases with temperature according to the law

$$\frac{d\ln p_1}{dT} = \frac{\lambda_1 + \frac{dQ_1}{dx}}{RT^2}. \qquad (6)$$

Here λ_1 is the latent heat of formation for the vapor of this component, and (dQ_1/dx) is its differential heat of solution. From a knowledge of λ_1 and the value of $\underline{p}$ for solutions of different concentration at a number of temperatures, the value of (dQ_1/dx) may be calculated for a series of solutions. Then, by the method of graphic integration, $Q_1 = \underline{f}(x)$ may easily be found, and $Q_2 = F(x)$ and (dQ_2/dx) may be obtained by fairly simple calculations.

In carrying out this calculation, we plotted our values for the partial vapor pressure of acetaldehyde in the form of log $\underline{p}$ against (1000/T) for a series of solutions (Fig. 6). Since the latent heat of vapor formation λ_{CH_3CHO} = 6000 cal/mole, values of (dQ_1/dx) for the different solutions may easily be obtained from the slopes of the lines in Fig. 6. It is clear from Fig. 6 that the value (dQ_1/dx) increases regularly as the concentration of the acetaldehyde solutions decreases. Having found the heat of solution $Q = \underline{f}(x)$ by graphic integration, we calculated the heats of formation of the solutions

$$CH_3CHO + xH_2O \quad (Q_2)$$

$$H_2O + xCH_3CHO \quad (Q_1)$$

The curves $Q_1 = \underline{f}(x)$ and $Q_2 = F(x)$ calculated in this manner are shown in Fig. 7.

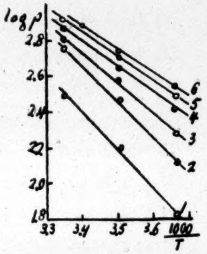

Fig. 6. Relation between partial vapor pressure of acetaldehyde and temperature. The straight lines 1,2,3,4,5 and 6 refer to aqueous solutions containing 10, 20, 30 50, 90, and 100 mole % of acetaldehyde.

As a check on the calculations, the formula giving the relationship between the temperature and total vapor pressure of binary solutions may be used:

$$\frac{d\ln p}{dT} = \frac{L}{RT^2} \qquad (7)$$

According to Vrevsky [19]

$$L = x'\lambda_1 + (1-x')\lambda_2 + x'\frac{dQ_1}{dx} + (1-x')\frac{dQ_2}{dx} \qquad (8),$$

where x' is the mole fraction for vapor; λ_1 and λ_2 are the latent heats of evaporation, and (dQ_1/dx) and (dQ_2/dx) are the differential heats of solution of the components.

TABLE 6

Comparison of Calculated and Experimental Heats of Formation

Composition of solution, %	Composition of vapor, x'	$\frac{dQ_1}{dx}$	$\frac{dQ_2}{dx}$	$L_{calc.}$ (cal/mole)	$L_{Expt.}$ (cal/mole)
10	0.94	3900	400	9950	10100
20	0.97	3000	800	9050	8950
30	0.975	1900	1200	7980	8050
50	0.98	600	2000	6700	6600
90	0.99	100	3000	6200	6270

The results calculated by means of this formula are compared in Table 6 with the $L_{Expt.}$ values, determined experimentally.

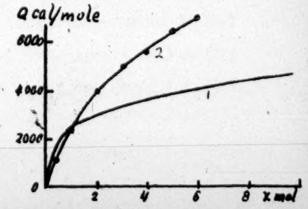

Fig. 7. Heat of solution curves for aqueous acetaldehyde solutions. 1) $H_2O + xCH_3CHO$; 2) $CH_3CHO + xH_2O$.

As will be seen from Table 6, the values of $L_{Expt.}$ and $L_{Calc.}$ do not differ by more than 1.5 %.

Unfortunately, we are not aware of any work on the determination of the heat of formation of acetaldehyde solutions; it was therefore not possible to compare our values calculated from vapor pressure measurements with values determined calorimetrically.

SUMMARY

1. The vapor pressures of a series of aqueous acetaldehyde solutions have been determined by a static method within the temperature range 0 to 25°.

2. The composition of the vapor of a series of aqueous acetaldehyde solutions has been determined by a dynamic method.

3. The method of Bose has been used to calculate the partial vapor pressures of acetaldehyde and water for solutions of $CH_3CHO + H_2O$ at various temperatures.

4. Heats of formation of aqueous acetaldehyde solutions have been calculated from vapor pressure measurements.

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ELECTRON MICROSCOPIC INVESTIGATION OF CHANGES IN THE SURFACE OF SOLID CATALYSTS DURING OPERATION

A. B. Shekhter and I. I. Tretyakov

In catalysis several factors are known which point to the extensive change in solid contacts during operation. The most striking of these is the well-known disintegration or, after long operation, complete destruction of platinum gauze in the oxidation of ammonia under industrial conditions; the roughening of the smooth surface of copper during the decomposition of ammonia [1] has also been described. The ordinary microscope when used for the investigation of these phenomena did not make it possible to study small submicroscopic changes taking place on the surface of the operating catalysts, and did not permit any further development in the concept of the disintegration of the smooth surface in operation. In addition, this method only allowed changes which had already taken place to be recorded.

The development of modern electron microscopy with its high resolving power prompted us to utilize this method for the detailed study of the structure of catalyst surfaces in operation.

As is known, for an electron microscopic investigation of the surface of solid objects, use must be made of the well-known replica method, i.e., the making of very fine molds which accurately reproduce the relief of the surface studied*. We used colloidal replicas, shading for greater contrast by means of a molecular stream of chromium directed at an acute angle on the surface of the replica**.

The suitability of this method for the study of metallic catalyst surfaces and the entire agreement between the electron microphotographs of the replicas with the relief of the surfaces producing them has been shown already for a number of examples [2]. By the use of the electron microscope method, it has been shown that the surface of fresh palladium sheet is comparatively smooth, and has only slight irregularities before use, but after a long time in use, large protuberances in the form of crystal formations of different sizes are seen [2]. In these samples the extreme surface heterogeneity was striking; each field of view in the electron microscope was noted for its structural characteristics, and it was impossible to discern any order in the distribution of the randomly distributed crystals. These photographs permitted it to be established without doubt only that there was a general tendency for catalysts to change in operation, and especially to form crystalline formations on a previously smooth surface.

It was shown by special experiments that changes in the surface of palladium and platinum similar to those which occur in the catalytic reaction are not produced by the action of the components of the reaction mixture (oxygen and hydrogen) on the reaction product (water vapor) at the reaction temperature, or by heating the catalyst in vacuum to the same temperature. This is well shown on a large number of electron microscope and ordinary microscope photographs, from which, because of lack of space, we only give one example illustrating the effect of heating a polished palladium plate in vacuum at 600° (see Fig. 2). From the photograph it is evident that, although the sample surface shows boundaries between crystalline granules characteristic of the metal recrystallization processes, the polished marks on the surfaces are fully retained, and there are no traces of disintegration of the surface.

It may be considered as established that the disintegration of catalyst surfaces is definitely connected with the catalytic reaction itself.

EXPERIMENTAL

For a detailed study of the early stages of the gradual disintegration of the operating surface of palladium and platinum, further experiments were carried out on the process of hydrogen oxidation on polished sheets of metal. The sheets were polished on a shammydisk, using chromium oxide; after polishing, the metal surface acquired a characteristic and easily reproducible form which facilitated the observation of small changes in the surface structure of the catalysts*.

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* The degree of accuracy of reproduction of the replica of small relief details of the surface depends on the type of replica employed; in our case the accuracy was approximately 100 A.

** As a result of "shading", the protuberances on the replica surface reflect a shadow, as the chromium is prevented from falling on the corresponding areas of the surface. Moreover, on those parts of the surface which form different angles with the molecular stream, films of chromium having different thicknesses are formed, and in the microphotograph they show various degrees of blackening.

The oxidation of hydrogen on platinum and palladium was carried out in the apparatus shown in Fig. 1. A measured stream of explosion mixture diluted with nitrogen was passed through the reactor 1. The catalyst, in the form of metallic sheets 4, 4.5 by 9 mm and 0.3 mm thick connected to a platinum-platinum-rhodium thermocouple sealed in glass, was placed in the reactor perpendicular to the gas stream. The reactor was surrounded by the furnace 3, the temperature of which was kept constant and uniform at 160° in all experiments by means of a thermoregulator.

The rate of the catalytic reaction was varied by changing the velocities of the gas stream and the degree of dilution by nitrogen of the stoichiometric mixture of hydrogen and oxygen. The rate of the mixture stream changed within the range of 1.2 to 5 liters per hour, and the nitrogen content in this mixture from 20-85%.

TABLE

Catalyst Temperature at Various Reaction Velocities

Catalyst	Nitrogen in mixture, percent	Total rate of mixture stream, liters per hour*	Catalyst temperature, °C	Duration of expt., in hours	Disintegration of catalyst surface
Palladium	85	1.2	250	40	None
	70	1.5	350	19	"
	43	2.3	450	3	Considerable
Platinum	25	4	600	5	"
	20	5	650	3	"

*The velocity of the nitrogen stream in all experiments was one liter per hour

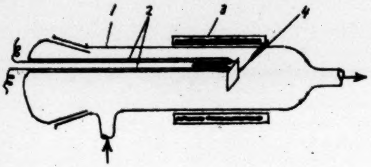

Fig. 1. Diagram of reaction apparatus.

Because of the exothermic hydrogen-oxidation reaction, the temperature of the metallic catalyst was higher than the temperature of the surrounding furnace (160°), and rapidly increased with an increase in the reaction rate (see Table).

By the selection of suitable mixtures and velocities, it was possible to find experimental conditions under which heating, as shown above, did not cause material changes in the surface, but the catalyst reaction itself produced sufficiently rapid characteristic rearrangements of the catalyst surface. Table 1 shows that these conditions were observed: for 43% nitrogen in the mixture, a total stream velocity of 2.3 liters per hour for palladium; and with 24% nitrogen in the mixture, a stream velocity of 4 liters per hour for platinum. Several series of experiments were carried out under these conditions to study the gradual disintegration of polished palladium and platinum.

The catalysts, after they had been working for a definite time interval, were removed from the reaction apparatus and replicas were made from them, after which they were replaced for further operation; as has been shown above, the contact activity did not noticeably change when a colloidal replica was made. The series of experiments showed mainly that the surface of the operating catalyst loses abrasions — traces due to polishing. This is illustrated by the photograph of polished palladium after three hours working (Fig. 3). Furthermore, the main part of the smooth catalyst surface became wavy (Fig. 4, photograph of platinum after 5 hours); then, after further work, the wavy surfaces acquired an angular character, and gradually formed a step-like crystalline structure [see photograph of platinum after 10 hours (Fig. 5) and after 15 hours (Fig. 6), and palladium after 20 hours (Fig. 7)].

We note that on the polished surfaces, which were apparently homogeneous up to the time of working, a sharp heterogeneity in the surface disintegration was observed after operation. As well as a more or less large disintegrated area of the surface, completely smooth areas were also encountered. In Figs. 8, 9, 10, 11, and 12, several of the different types of surface disintegration observed are shown. As a rule, the areas characterized

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*In order to remove aberrations in the metal structure arising from previous mechanical treatment, the samples were tempered before being polished by heating for a few minutes to 1200° in the case of platinum, and to 800° in the case of palladium.

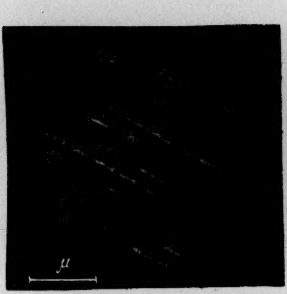

Fig. 2. Polished palladium sheet heated in vacuum at 600°. X 16,000.

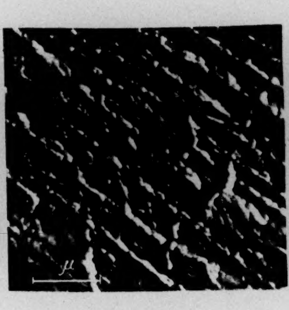

Fig. 3. Polished palladium catalyst after 3 hours in operation. X 16,000.

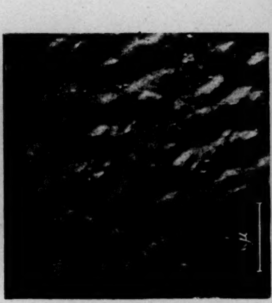

Fig. 4. Polished platinum catalyst after 5 hours in operation. X 16,000

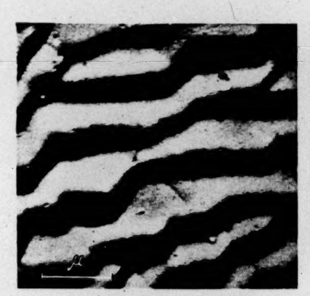

Fig. 5. The same catalyst after 10 hours. X 16000.

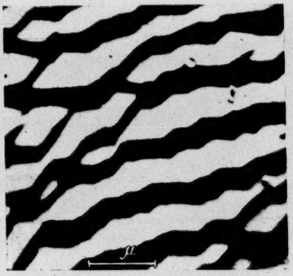

Fig. 6. The same catalyst after 15 hours. X 16,000.

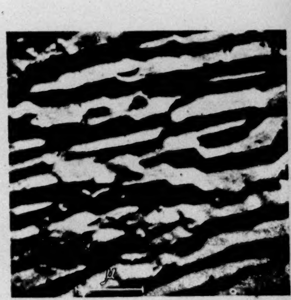

Fig. 7. Polished palladium catalyst after 20 hours in operation X 16,000.

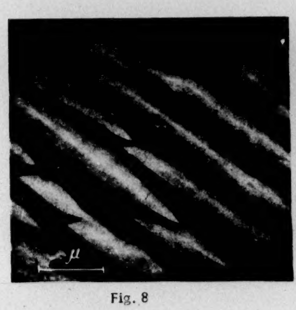

Fig. 8

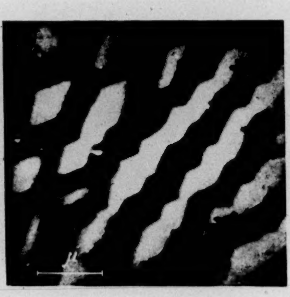

Fig. 9

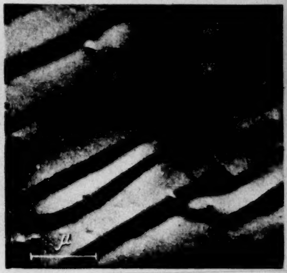

Fig. 10

Fig. 8, 9, 10, 11, 12 (11 and 12 are on the following page): Different parts of a platinum catalyst after 15 hours in operation. X 16,000.

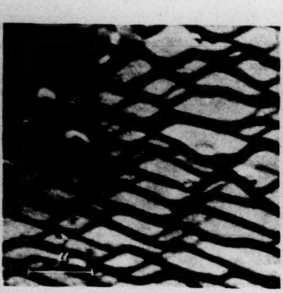

Fig. 11. Caption on previous page.

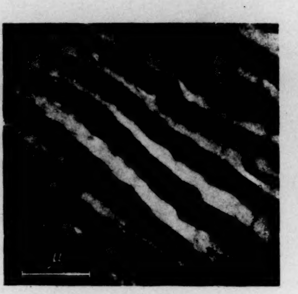

Fig. 12. Caption on previous page.

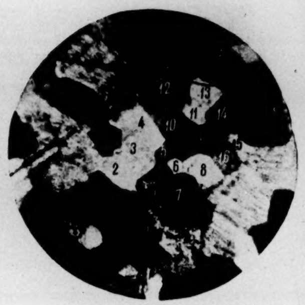

Fig. 13. Visual photograph of platinum catalyst after 15 hours in operation X 170.

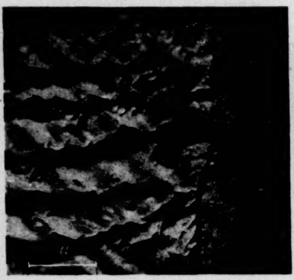

Fig. 14. Boundaries between different zones on an operating palladium catalyst. X 16,000.

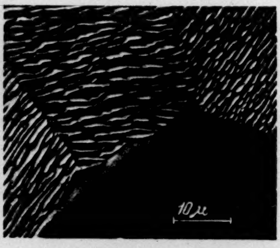

Fig. 15a. Different disintegration zones on a platinum catalyst after 150 hours in operation.

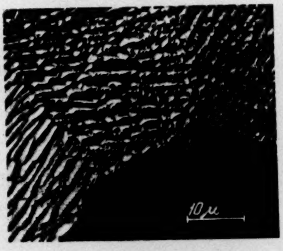

Fig. 15b. The same zones after 440 hours of catalyst operation.

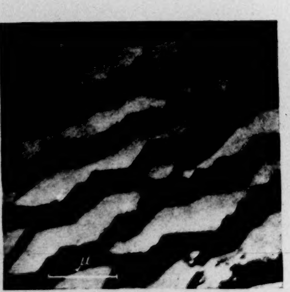

Fig. 16. Part of zone No. 8 on platinum catalyst after 15 hours in operation. X 16,000

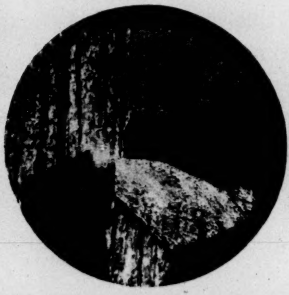

Fig. 17. Visual microphotograph of platinum-rhodium catalyst after 82 hours in operation at 600° X 310.

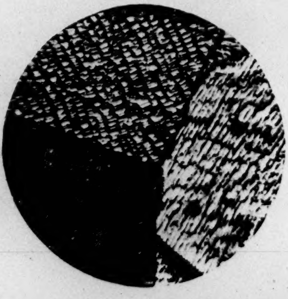

Fig. 18. Visual microphotograph of copper catalyst after 30 hours in operation at 470° X 310.

by one or the other type of disintegration, are too large to be placed on the field of view of the electron microscope (~0.01 mm^2), and for this reason their distribution on the catalyst surface was studied on a visual microphotograph with magnification of ~200. In the microphotographs obtained in this way, it is seen that the surface of the working catalyst has well-bounded zones possessing irregular polygonal features. The nature of the surface disintegration inside each "zone" is the same for all the "zones" but individual "zones" differ considerably in the characteristics of their surface structure [3].

Figure 13 shows a visual photomicrograph (magnification 170) of a polished platinum plate after 15 hours operation in explosion mixture, diluted with 25% of nitrogen, at 600°. On this, individual marked "zones" are visible, and in spite of the small magnification it is possible to note differences in the nature of the disintegration in different "zones". The picture seen directly in the visual microscope looks more effective than the photograph, because different "zones" showed different colorings (blue, light blue, orange, green, brown, and other tints). The "zone" size varied from about 0.01-0.2 mm in cross section. It is obvious, therefore, that in the electron microscope, in which the magnification is 10,000 and the field of view equal to 5 X 5 μ^2, it is impossible to see more than one "zone" entirely, and either a small part of a "zone" or the boundary between two neighboring "zones" with the adjoining regions is observed (for example, Fig. 14, photograph of the boundary between two "zones" on the surface of a platinum catalyst after operation).

In order to follow the gradual changes in individual zones with the aid of the electron microscope, it would be necessary to be able to take repeated photographs of replicas of the same submicroscopic areas. This problem is very difficult if the usual methods of making replicas are employed, and therefore the development of a special technique was necessary [4].

By the use of this technique, which allowed the repeated taking of replicas of given submicroscopic regions, it was possible to follow the successive stages in the disintegration of individual "zones"; for example, photographs in Figs. 4, 5, and 6 were made from the same zone denoted by the number 4 in Fig. 13, after the platinum catalyst had been working for 5, 10, and 15 hours. It was also possible to compose an electron microscope picture of the deposition of individual "zones" on the surface area examined.

Fig. 15 shows a small part of this electron microscope picture of a platinum surface after 15 hours (Fig. 15 a) and after 440 hours of working (Fig. 15 b). These photographs were taken with a magnification of 2000, and partly embrace 4 "zones". Although 3 "zones" in this surface acquired a marked crystalline character, one of these remained comparatively smooth after 440 hours.

The surface disintegration of platinum catalysts was followed in stages over a long period; it was thus shown that after 1000 hours working, the surface continues to disintegrate under the influence of a chemical reaction. It is of interest that several "zones" comparatively distant from one another, show extraordinarily similar structures (see, for example, in Figs. 6 and 16, the electron microphotographs of "zones" denoted No. 4 and No. 8 in the visual microphotograph Fig. 13). This gives rise to the impression that different "zones" disintegrate in different ways, but that the number of types of disintegration is fairly limited.

As visual microphotographs of platinum and palladium sheets after use show, their appearance in the visual microscope is very similar to the appearance of the same sheets after etching [3]. In both cases, the polishing marks (abrasions) disappear and individual areas or "zones" bounded from one another make their appearance.

It seems probable that the zones appearing on the metal surface in both cases are due to the same cause; in other words, the catalytic reaction exposes the crystalline structure of the metal in the same way as etching, and "zones" appearing correspond to the boundaries of the individual crystals making up the platinum surface.

The following experiment may be considered as confirmation of this idea. A polished palladium sheet was first etched with nitric acid and then used as a catalyst in the oxidation of hydrogen. After 10 hours, it was found that the zone boundaries (different in character from the disintegrated surface) accurately corresponded to the boundaries between the crystals which had appeared on etching [3]. The changes in the catalyst surface under the influence of the catalytic reaction described above suggest an extensive rearrangement in this surface, which can only be brought about if it is assumed that there is an intensive lateral movement of the catalyst surface atoms.

Experiments in which palladium and platinum were heated in vacuum in the individual components of the reaction mixture (to 1000°), showed that the cause of this increased lateral movement was not the increase in temperature which took place in our experiments. (Up to 450° in the case of platinum and up to 600° in the case of palladium). Consequently, the cause of this movement must be different and must be connected with the catalytic reaction itself; so, for example, the appearance of energy necessary to increase lateral movement may be connected with the action of active intermediate products formed in the reaction or with the formation of unstable catalytic compounds which leave the lattice of the metal on the surface layer in a disturbed condition on decomposition.

Differences in the disintegration of individual "zones" under the action of the catalytic reaction are striking. This leads to the idea that different zones (evidently representing different boundaries of the crystal surface) have different catalytic activities. Thus, the experimental work given above may be of interest in connection with one of the most important problems of catalysis theory, the problem of the distribution of active centers on the catalyst surface; however, this picture may also be obtained as a result of differences in the stability of the different crystal boundaries which make up the surface toward disintegration.

The choice between these two explanations can only be made, evidently, on the basis of results of catalytic activity measurements on individual boundaries of a sufficiently large mono-crystal. In this connection, we have undertaken a study of the catalytic activity of the boundaries of mono-crystals.

Experiments on the oxidation of hydrogen at 430° on the individual boundaries of a specially-grown large copper monocrystal in a gas stream containing 98.5 % hydrogen and 1.5% oxygen showed that the reaction yield (per unit of surface) was approximately the same for boundaries (100), (110), and (111), while for boundaries (100) and (110)the reaction developed in a different manner and for boundary (111) it remained smooth during the course of the whole experiment (23 hours). This evidently points to the fact that there is no unambiguous correlation between the disintegration of surfaces and their catalytic activity.*

The disintegration of solid catalysts during reaction is not limited to the examples given above, but is apparently a more general effect which applies to a wide range of catalysts and processes, and to these belong a number of systems in which the changes have not been known up to now. When hydrogen is oxidized on solid copper and ammonia on platinum or platinum-rhodium alloys, we succeeded, with the aid of the electron microscopic methods, in observing extensive disintegration of the surface similar to that described above for platinum and palladium in the oxidation of hydrogen. With platinum-rhodium alloys the disintegration depends on the percentage of rhodium in the alloy.

This disintegration, which is shown by the appearance of crystal structures on the initial smooth catalyst surface, has also a zonal character (Fig. 17 — platinum-rhodium catalyst after operation and Fig. 18 — copper catalyst after operation; both photographs were made with a magnification of 310). Changes in the structure of the smooth surface of iron catalysts in the decomposition of ammonia were also observed.

SUMMARY

1. The data given in this paper show that the changes in solid metallic catalysts during operation are of much wider occurrence than has generally been considered up to now.

The metallic catalysts (Pt, Pd, Cu, Fe, alloys of platinum and rhodium) undergo characteristic and fairly complex changes in surface structure from the very beginning of operation, and these changes continue even during long periods of operation.

2. When catalytic reactions are carried out on tempered, polished, solid metallic catalysts, the electron-microscope method enables qualitative differences in the disintegration of the individual crystal boundaries which go to make up the polycrystalline surface to be observed ("zonality" of disintegration).

3. A parallel study of the disintegration and catalytic activity of the individual boundaries of a copper monocrystal in the oxidation of hydrogen showed that there is no well-defined functional relationship between the degree of disintegration in this reaction and the catalytic activity. Thus, it is impossible to draw conclusions about the catalytic activity of these surfaces from the differences in the disintegration of the boundaries in the reaction.

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* In the same way, it is possible to interpret the experimental results of Leidheiser and Gwathmey [5], who studied the oxidation of hydrogen at the boundaries (100) and (111) of a copper monocrystal under somewhat different kinetic conditions; they observed a higher catalytic activity at the undisintegrated boundary (111).

PROBLEMS OF THE CHEMISTRY AND TECHNOLOGY OF MINERAL FERTILIZERS IN CENTRAL ASIA*

S. I. Volfkovich

Progress in chemistry and biology and the deep interpenetration of these sciences is having an increasing effect on crop productivity. In recent years considerable successes have been achieved in the study of the nutrition cycle of elements , the assimilation and metabolism in plants, and in elucidating the functions of microorganisms and microelements. Our knowledge of functions of organic substances has been extended. Growth stimulators and growth suppressors have been discovered, synthesized, and introduced into practice. Some of these have been used to counter weeds (herbicides) and plant diseases (fungicides).

Many new and important developments in this borderland region between chemistry and biology have been introduced by Soviet scientists and agriculturists. Naturally, all this work, which is directed toward the achievement of an abundance of food products and industrial raw materials, makes a direct contribution to the building of Communism.

The further development of the chemistry, technology, and agricultural chemistry of fertilizers is of especially great significance in the republics of Central Asia, where the agricultural industries, using the products of the chemical industry on the basis of the achievements of Soviet agriculture, biology, and technique, have already made considerable progress. In his Report to the 19th Party Congress, Comrade Malenkov, mentioning the especially rapid rate of growth in the production of cotton and of sugar-beet in the post-war period, gave a highly authoritative appraisal of this progress. Comrade Beriya in his speeches to the 19th Party Congress, pointing out the achievement of the Soviet Eastern Republics in producing a harvest on the average of 21 centners of raw cotton per hectare, said: " In no cotton-producing country in the world is such a yield achieved as is reached by Soviet cotton pods. In 1951 the productivity of cotton in Egypt was 11.5 centners per hectare, in the United States 8.3, in India 3.4, in Pakistan 5.2, in Turkey 7.2, and in Iran 4.5 centners per hectare. It should be taken into account that the high yield of cotton in the Soviet Eastern Republics is obtained over large areas, which is borne out by the fact that the Soviet Republics mentioned produce as much cotton as India, Egypt, Iran, Turkey, and Afghanistan taken together" **.

The agricultural industry of the Central Asian Republics is noted for its extensive utilization of chemistry, for its high standards in the use of fertilizers for cotton, and for its high efficiency. There have been years in which fertilizers have been applied in insufficient quantities and in unsuitable forms, or with disproportionate relationships of nutritive elements, without considering the type of soil or manner of cultivation. In these years productivity was considerably reduced.

These circumstances make it necessary for chemists and agricultural chemists to consider the urgent problems arising in the further planned and purposeful study of the optimum conditions for the application of fertilizers in central Asia, and also the most suitable conditions for production of these fertilizers, taking into account the local conditions and sources of supply.

The 19th Congress of the Communist Party of the Soviet Union in its directives on the Five-Year Plan stipulated that in1955 the value of the production of raw cotton should be increased 55 to 65% in comparison with 1950. In the districts of Central Asia and Southern Kazakhstan the cotton harvest is to be increased to 26 to 27 cent centners per hectare.*** In the section devoted to the development of the chemical industry, the Directives of the 19th Party Congress called for a greater rate of increase in the production of mineral fertilizers.

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* Paper read at a combined session of the Division of Chemistry of the Academy of Sciences, USSR, and the Academy of Sciences of the Uzbek SSR, October 24, 1952, Tashkent.

** Address of L. Beriya at the 19th Congress of the All-Union Communist Party (Bolsheviks), State Political Press, 1952, page 16.

*** See Directives of the 19th Party Congress on the 5th Five-Year Plan for the Development of the USSR in 1951-1955. Pravda Press, Moscow, 1952.

For Central Asian irrigated agricultural land, the mineral fertilizers which are of the greatest importance are nitrogen and phosphorus fertilizers. These are the most effective. Potassium fertilizers are considerably less effective since most of the soil in Central Asia (gray desert soil) contains sufficient quantities of potassium, easily accessible for the plants. Potassium manuring is satisfactory only on meadow soils rich in organic substances and poor in lime, and then with liberal applications of nitrogen. Lime fertilizing is ineffective on the alkaline soils of Central Asia. Gypsum may acquire considerable importance as a chemical treatment for the saline soils which are encountered in various districts. In recent years field experiments by Soviet research institutes have established the effectiveness applying boron and manganese micro-fertilizers to cotton and alfalfa plants.

It is generally considered that the application of mineral fertilizers should be accompanied by the application of orgnaic fertilizers, of which cottonseed meal, dung, and in some districts peat are the most widely distributed and the most effective in Central Asia, both alone and as mixtures with mineral fertilizers. According to the data obtained in field experiments by the Central Asian Institutes and Geographical Stations of the Scientific Research Institute for Fertilizers and Insecticides (NIUIF), the approximate requirements per ton of nutritive element are: for the cotton plant, 1 ton of nitrogen per 12 to 14 tons of raw cotton, and 1 ton of P_2O_5 per 6 to 7 tons of raw cotton; and for alfalfa, 1 ton of P_2O_5 per 20 to 30 tons of hay.

The amount of fertilizers to be applied per hectare of sown area and the proportion of the nutritive elements in the fertilizer for the basic Central Asian cotton crop are different for different soils and conditions of cultivation.

Conventionally, for calculating the manure requirements in Central Asia, some technical-economics papers take the following averages: for cotton 100 to 110 kg nitrogen per hectare, 75 kg P_2O_5 per hectare, and 25 kg of K_2O per hectare; and for alfalfa, 76 kg P_2O_5 per hectare, and 25 kg K_2O per hectare. For complex and mixed fertilizers, agrochemists recommend a basic pre-seed fertilizer of approximately the following composition: $N:P_2O_5 = 1:1$; 1:2; and 1:3, and as a supplement with predominant nitrogen, approximately 2:1 and 1.5:1*.

The presence in the Central Asian Republics of large deposits of phosphates, sulfur, sulfide minerals, and potassium, and other salts, as well as water power and fuel resources, together with the large demand for fertilizers of high efficiency raises chemical problems, both pure and applied, the solution of which should ensure further developments in the production of mineral fertilizers and the utilization of chemicals in agriculture.

A little more than 25 years ago (in 1926) in Southern Kazakhstan in the ancient deposits of the Middle Cambrian growth of the Kara-Tau mountain range, Soviet geologists discovered large deposits of phosphorites of the blanket type [1], which were unknown up to that time in our country. In size of the blankets, their productivity, and extent of reserves, these phosphorite deposits are superior to any hitherto found in our country, being inferior only to Khibinsk apatites. However, they have the great advantage over these that they occur close to the important fertilizer-consuming districts of Central Asia. A disadvantage of the Kara-Tau phosphorites is their considerable variation in the content of phosphorus, silicon, magnesium, and other components from blanket to blanket, and in their comparatively high magnesium content, which affects the sulfuric acid treatment in the manufacture of superphosphates and concentrated phosphoric acid.

The finely dispersed structure and close growth of the minerals greatly hampers the mechanical and flotation enrichment of these phosphorites. Being metamorphosed apatites, the Kara-Tau phosphorites, as distinct from other organogenic phosphorites, cannot be used as direct fertilizers, especially on alkaline soils. Superphosphate prepared from the lower grades of these phosphorites is hygroscopic, and under unfavorable climatic conditions, forms cakes. The concentration of phosphoric acid obtained from these phosphorites is also difficult because of the separation of salt precipitates.

In recent years in the NIUIF, the Kazakh Academy of Sciences, and other scientific institutes, practically all the possible methods for the chemical conversion of the Kara-Tau phosphorites into fertilizers have been studied. Detailed studies have been made of the mineralogical and petrological composition, the structure and physical properties of these phosphorites, with the aid of crystal optical analysis, thermography, X-ray, and electron microscopy; several systems have been studied connected with the chemical decomposition of these phosphorites.

As a result of numerous investigations and pilot plant experiments, it may at present be considered established that the best methods for the chemical treatment of these phosphorites are the following:

1) The production of concentrated fertilizers—precipitated dicalcium phosphate, ammofos (a mixture of di- and mono ammonium phosphates), etc.

2) The production of ammoniated superphosphate by neutralizing the free acid with ammonia or ammon-

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* Further experimental work should be done to determine exactly the optimum proportions of the nutrient elements.

ium salts (solution of nitrate of ammonia or other nitrogen-containing salts of ammonia).

3) The production of citrate-soluble phosphates by non-acid (thermal and alkali) processes: of meta- and pyrophosphates, fused and alkaline phosphates, etc.

The fertilizers enumerated may be obtained by various chemical processes. In the present short report it will be useful to consider only those processes in which phosphorites are treated with sulfuric acid, since these processes are the most widely used and are the predominant ones in our chemical industry. They include the production of superphosphate, phosphoric acid, and the concentrated fertilizers enumerated under (1) above. At the present time, as a sulfur-containing raw material there may be utilized sulfur, sulfides, sulfurous gases from nonferrous metallurgy, gypsum, alunite, and others. It is possible to regenerate sulfuric acid in the production of concentrated fertilizers as a result of the thermal decomposition of phospho-gypsum, with the production of sulfurous gases and cement.

The fundamental task of our superphosphate industry is the raising of the quality and especially of the physical properties of superphosphate obtained from the Kara-Tau phosphorites by concentrating the raw material, granulation [2], or ammoniation of superphosphate by ammonia. When superphosphate is ammoniated by means of ammonium salts, for example liquid ammonia and ammonium nitrate, phosphorus-nitrogen fertilizers with proportions of nutrient elements close to that required for basic pre-seed applications may be obtained.

It is sometimes thought that the application of concentrated fertilizers containing 2, 3, or 4 times more nutrient substances than the ordinary low-percentage fertilizers, such as superphosphate, ammonium sulfate, and others, is only an urgent production task for the most remote regions, such as the Kola Peninsula, from which apatite is transported to the Ukraine, the Caucasus, and to Central Asia. This results in an economy of milliards of ton-kilometers. However, this problem is also of great importance for the Central Asian Republics, because the distance from the Kara-Tau phosphorite deposits to many regions which consume fertilizers varies from a few hundred to fifteen hundred kilometers. Moreover, the use of concentrated fertilizers results in a saving in freight transportation, in work of applying the fertilizer to the soil, and also in packing and storage. All these taken together are very important, as is shown by economic calculations, under Central Asian conditions. Therefore, in the near future it will be advantageous to construct factories for the manufacture of concentrated fertilizers—ammofos, precipitated dicalcium phosphate, etc., in the Central Asian Republics.

The most concentrated and the most rapidly acting fertilizer which is of considerable interest in the fertilizing of the cotton plant (especially as a supplement) is ammofos, which contains about 50% P_2O_5 and about 14% nitrogen. This fertilizer, according to the results of Chumanov's experiments [3], is highly effective on gray desert soils, thanks to the mobility of this form of nitrogen-phosphate fertilizer in soils when it is applied at the time of vegetation (supplement). Moreover, the production of ammofos from the Kara-Tau phosphorites is one of the most efficient methods of working these phosphorites. The technology of the production of ammofos from apatite concentrates on an industrial scale has been mastered in our country.

As far as precipitated dicalcium phosphate is concerned, its preparation, from the economic point of view, is most efficiently carried out by the nitric acid or the hydrochloric acid decomposition of phosphate. The hydrochloric acid treatment of phosphates is efficient when effluent or very cheap hydrochloric acid is available. This gives calcium chloride as a by-product, which is troublesome and difficult to use [4]. Methods of utilizing it with the possible reversible production of hydrochloric acid have been proposed.

The decomposition of phosphates by nitric acid with the subsequent preparation of precipitated dicalcium phosphate and potassium and ammonium nitrates [5] seems to be one of the most promising for Central Asian technological conditions. These processes are based on the following main reactions:

$$Ca_5F(PO_4)_3 + 10\,HNO_3 = 3H_3PO_4 + 5Ca(NO_3)_2 + HF \qquad (1)$$

$$H_3PO_4 + Ca(NO_3)_2 + CaCO_3 = CaHPO_4 + Ca(NO_3)_2 + CO_2. \qquad (2)$$

By the interaction of calcium nitrate and ammonium carbonate (or of ammonia and carbon dioxide), ammonium nitrate and calcium carbonate may be obtained.

$$Ca(NO_3)_2 + (NH_4)_2CO_3 = 2NH_4NO_3 + CaCO_3. \qquad (3)$$

In a subsidiary reaction, accompanying the main reactions in which phosphate is decomposed by nitric acid (1) and (2), hydrofluosilicic acid (4) is formed. It is precipitated with the aid of sodium nitrate (or soda) in the form of sodium silicofluoride (5)

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O. \qquad (4)$$

$$H_2SiF_6 + 2NaNO_3 = Na_2SiF_6 + 2HNO_3. \qquad (5)$$

In the nitric acid treatment of phsophates, the raw material is fully utilized; instead of waste products which are obtained in the sulfuric acid extraction of phosphoric acid (so-called phospho-gypsum) and in the hydrochloric acid decomposition of phosphates (calcium chloride), in the nitric process a fertilizer, calcium nitrate, is obtained. Thus, in this process, the nitric acid is used in a two-fold manner: for the decomposition of the phosphate and for combination with the calcium to form nitrate. In view of the fact that calcium nitrate is less effective than ammonium nitrate as a fertilizer on Central Asian soils, calcium nitrate can be converted to ammonium nitrate by means of ammonium carbonate according to the equation given above (3).

A number of our workers have developed several chemical technological processes for the nitric acid treatment of phosphates, not only for the separate preparation of dicalcium phosphate and calcium nitrate, but also for the preparation of double (nitrogen-phosphorus) and triple (nitrogen-phosphorus-potassium) fertilizers. An example of such a process is the interaction of nitric acid extracts with ammonium or potassium salts (without separating the products of reaction), as a result of which the triple fertilizer "azofos" (abroad "nitrophos") is directly obtained. Equation (6) schematically represents this process.

$$H_3PO_4 + Ca(NO_3)_2 + 2NH_3 + K_2SO_4 = CaHPO_4 + 2NH_4NO_3 + K_2SO_4 \qquad (6)$$

The processes in which phosphates are decomposed by mixtures of sulfuric and nitric acid, or mixtures of nitric and phosphoric acids, with the production of a solid phosphorus-nitrogen fertilizer, similar to the production processes for superphosphate (Equations 7 and 8) are also of interest:

$$2Ca_5F(PO_4)_3 + 6HNO_3 + 4H_2SO_4 = 3CaH_4(PO_4)_2 + 3Ca(NO_3)_2 + 4CaSO_4 + 2HF \qquad (7)$$

or

$$CaF(PO_4)_3 + 6HNO_3 + 2H_2SO_4 = 3H_3PO_4 + 3Ca(NO_3)_2 + 2CaSO_4 + HF. \qquad (8)$$

The fertilizers obtained here, however, contain relatively small amounts of N and P_2O_5.

Other processes for the production of nitrogen-phosphorus fertilizers which could be used by industry without change of apparatus are also being studied. The future use of these processes, as well as the successful solution of the technical problems involved, depends also on how the proposed new forms of complex fertilizers will meet the requirements of agricultural chemistry with regard to the N and P_2O_5 ratio.

Technical-economic and planning estimates show that the processes for the treatment of phosphates with nitric acid should yield phosphorus fertilizers 25-35% cheaper than those obtained by the sulfuric acid methods. Naturally, where nitric acid is being used for the production of nitrates it will be economical to carry out as subsidiary work the decomposition of phosphates and the production of calcium nitrate. In a number of countries the industry has already developed along these lines, and many large factories are already in operation. It should be mentioned that the nitric acid method allows the utilization of lower grade phosphorites than is possible in the sulfuric acid methods, and fluorides are obtained as by-products.

A second promising method, which is of importance for Central Asia, is the electrothermal working of phosphates for the preparation of phosphorus, phosphoric acid, and concentrated fertilizers, as well as phosphates for use as live-stock feeds. The fundamental reactions of this process have been studied in detail by NIUIF, and our industry is already familiar with them [6, 7, 8, 9, 10]. Our country was one of the first to master the process of the electrical sublimation of phosphorus from low-grade phosphorites, and to carry out a deep study of the numerous theoretical problems in the field of the mechanism and kinetics of processes connected with this technique, and also the complex process for the preparation of phosphorus with the simultaneous utilization of gases, slag, and ferrophosphor. Below we give the basic reactions of the process for the sublimation of phosphorus from phosphates with the subsequent oxidation of phosphorus and the preparation of phosphoric acid.

$$2Ca_5F(PO_4)_3 + 15C + nSiO_2 = 3P_2 + 15CO + 9CaO \cdot nSiO_2 + CaF_2 - 838 \text{ kcal}. \qquad (9)$$

$$2P_2 + 5O_2 = P_4O_{10}. \qquad (10)$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4. \qquad (11)$$

Reaction (9) is accompanied by the absorption of heat — it is strongly endothermic — but reactions (10) and (11) are accompanied by the evolution of heat — they are exothermic. This presents an opportunity to save electrical energy in the process of phosphorus sublimation

By the interaction of vapors of metaphosphoric acid with lime or phosphates, it is possible to obtain a high-percentage phosphorus fertilizer — calcium metaphosphate — containing up to 66% P_2O_5. The method was first proposed here by Britske [8]:

$$2HPO_3 + CaO = Ca(PO_3)_2 + H_2O \tag{12}$$

or

$$4HPO_3 + Ca_3(PO_4)_2 = 3Ca(PO_3)_2 + 2H_2O\ . \tag{13}$$

An interesting and promising variant is the oxidation of phosphorus by water vapor or liquid water, with the production of elementary hydrogen. This has been studied in NIUIF and in the State Institute of High Pressures, on the basis of the following reaction:

$$P_2 + 5H_2O = P_2O_5 + 5H_2\ . \tag{14}$$

The hydrogen separating in the furnace, together with the phosphorus, also reacts with the water vapor to form hydrogen and carbon dioxide:

$$CO + H_2O = H_2 + CO_2\ . \tag{15}$$

Further, hydrogen combines with nitrogen to form synthetic ammonia:

$$N_2 + 3H_2 = 2NH_3\ . \tag{15 a}$$

By the interaction of ammonia and phosphoric acid, ammonium phosphate may easily be obtained:

$$H_3PO_4 + NH_3 = NH_4H_2PO_4\ . \tag{16}$$

The result is a combination of two important chemical processes — the preparation of phosphorus and phosphoric acid, and the synthesis of ammonia. As a result of the combination there is a saving in electrical energy in the preparation of hydrogen, since this is obtained from the energy of oxidation of the phosphorus by water. This complex of processes is of interest not only because the development of hydroelectic construction makes possible the raising of this question, but also because the electrochemical method permits the utilization of low grade phosphate raw materials and the preparation of highly concentrated and pure phosphoric acid, which facilitates and simplifies its further industrial treatment and conversion to concentrated fertilizers.

Other thermal and thermal-alkali methods for the treatment of phosphates, for example, baking or fusing with natural alkalies, salts or magnesium silicates, the treatment of phosphates with water vapor under high temperature for the removal of fluorine, the preparation of metaphosphates and pyrophosphates, and so on, should be evaluated, not only from the point of view of their technical and economic suitability for production from local raw materials, but also for their agricultural chemical efficiency. Large scale field trials on citrate-soluble types of fertilizers have not yet been carried out on Central Asian soils.

The following are the main reactions on which these processes are based:

The preparation of thermophosphates*:

$$2Ca_5F(PO_4)_3 \underbrace{+ 3Na_2CO_3}_{(3Na_2S + SO_2)} = 2Na_2O \cdot 10CaO \cdot 3P_2O_5 + 2NaF + 3CO_2. \tag{17}$$

The preparation of fused magnesia phosphates:

$$Ca_5F(PO_4)_3 + 3MgO + 6SiO_2 = 4CaO \cdot 3MgO \cdot 3PO_4 \cdot 6SiO_2\ . \tag{18}$$

The defluorization of apatite:

$$2Ca_5F(PO_4)_3 + 2H_2O = Ca(OH)_2 \cdot 3Ca_3(PO_4)_2 + 2HF\ . \tag{19}$$

As can be seen, this reaction is accompanied by the displacement of fluorine from the crystal lattice of apatite, and its replacement by hydroxide. The latter process is of interest because the transformation of P_2O_5 into a form easily assimilated by the plant is carried out by a process in which the only chemicals used are water vapor and silica.

Of the nitrogen fertilizers, the most useful type is ammonium nitrate, the physical properties of which have markedly improved as a result of granulation and the introduction of modifying additives (the caking and hygroscopic properties are markedly reduced). In order to improve the physical properties, other formulas have been proposed, and also a number of variations of the industrial process. The organic additives which have been used for a number of years to improve the physical properties of ammonium nitrate have now been replaced by inorganic ones.

Because of their low efficiency, sodium and calcium nitrates are of lesser value on Central Asian soil than in other districts, and their low nitrogen content (12-17 %) in comparison with ammonium nitrate (35%) should stimulate the development of the latter.

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* In the Institute of Chemistry and Metallurgy of the Kazakh Academy of Sciences, Bekturov studied the preparation of thermophosphates by using sodium sulfate and carbon (i.e, sodium sulfite) instead of soda [11].

Until recently the production of calcium cyanamide (alkaline nitrogen fertilizer) has been regarded as uneconomical be cause of its high power requirements, its low nitrogen content (from 18 to 20%), and the necessity of taking precautions to avoid poisoning of animals where it is used. Since calcium cyanamide is not only a nitrogen fertilizer, but also a herbicide (an anti-weed agent), and in recent years has begun to be used successfully as a defoliant for cotton (it assures the rapid removal of leaves for the subsequent use of mechanical pickers) the question of the development of calcium cyanamide production on a large scale should be examined from the technical and economic points of view, with the prospect of new hydroelectric constructions being taken into consideration.

The development of the production of synthetic carbamide (urea), one of the most efficient and the most concentrated of the known nitrogen fertilizers, is mainly dependent on the development of the synthesis of ammonia, the subsidiary preparation of concentrated carbonic acid, and the economical production of urea and its solutions in liquid ammonia. These may be of interest as concentrated liquid fertilizers (having insignificant vapor tension in comparison with liquid ammonia), or as intermediates for the preparation of complex fertilizers and for the ammonization of superphosphate with the admixture of urea [12].

The most useful form of potassium fertilizers for Central Asia are those in the form of high-potassium-content salts—chlorides and sulfates, and in the future, possibly, potassium nitrates and phosphates. Potassium salts of low potassium content usually contain sodium chloride and other salts, which raise the saline content of the soil, which is naturally undesirable on saline soils.

Mixtures of fertilizers are advantageous, and for this it is necessary to ensure the neutrality of the phosphates used as components. For example, superphosphates should be previously neutralized with lime and ammonia before being mixed with ammonium nitrate. A suitable phosphate component of fertilizer mixtures is precipitated dicalcium phosphate, because of its neutrality, ease of dispersion, and good physical properties.

What are the main scientific and production tasks in the near future?

It is necessary to establish the efficiency on Central Asian soils of the citrate-soluble forms of phosphates contained in defluorized, fused and alkaline phosphates and also in meta and pyrophosphates, the production of which does not require the consumption of mineral acids and may be carried out even on phosphorites which are rich in magnesium carbonate and silicic acid. The study of this question should be related to theoretical investigations on the mobility of various forms of phosphates in gray desert soils and on their absorption by the plant; this depends on their degree of particle dispersion, which is connected with their granulation. Here, a theoretical investigation of the nutrient substances which are assimilated by plants(not connected with the soil) is of great interest. The study of the optimum proportions of nitrogen, phosphorus and potassium for pre-seed and supplementary fertilizers should be studied more intensely and in a more extended manner in order to solve the question of the production of complex and mixed fertilizers meeting the requirements of the cotton, alfalfa, sugar-beet, fruit and other crops.

An intensified study should be continued on organic mineral fertilizers based on the treatment of carbons, peat, plant cellulose and other natural organic materials with phosphoric and nitric acid, ammonia, and so on, in order to determine their efficiency, and especially to discover the part played by humus compounds as growth promoters. The problem of the combined use of fertilizers and growth stimulators is of great interest. The study of the requirements of Central Asian agricultural crops for microelements, boron, manganese, zinc, etc., should be continued. For a complete and rational utilization of the Kara-Tau phosphorites an all-around increase in the study of the methods for their mechanical and chemical enrichment should be carried out. As well as this, the study of the efficient production of thermal and alkaline phosphates should be intensified, especially thermal phosphates, fused phosphates, meta- and pyrophosphates and also defluorized phosphates. The use of local mineral resources as a supplement for cotton, and in order to reduce the transport costs over long distances, the production of "ammofos" from the Kara-Tau phosphorites, should be introduced in order to increase the physical properties of superphosphate; the mastering of the processes of ammonization by means of ammonia and ammonium salts should be hastened.

It is necessary that the production of dicalcium phosphate (precipitated) with the subsidiary preparation of ammonium nitrate from the nitric acid decomposition of the Kara-Tau phosphorites should be mastered. At the same time, the agricultural, chemical, and economic suitability of the double and triple fertilizers containing phosphorus, nitrogen, and potassium (of the types "azofos" or "nitrofos" in the granulated form) should be determined. Attention should also be paid to the study of the suitability of methods of producing nitrogen-phosphorus fertilizers by simplified technological processes in which the phosphates are decomposed by mixtures of nitric and sulfuric acids (similar to superphosphates).

A process which shows considerable promise is the electro-thermal treatment of unenriched Kara-Tau phosphorus obtained into phosphoric acid, concentrated fertilizers, and phosphates for foods and feed-stuffs. Here a detailed study is required for the processes in which phosphorus is oxidized by steam and by liquid water with the production of elemental hydrogen, and the subsequent synthesis of ammonia, with the object of combining the latter with phosphoric acid to form ammonium phosphate.

Investigation should be continued on the complex processes in which phosphorus is distilled with the simultaneous preparation of calcium carbide or earth-clay cement and also other methods for the utilization of carbon monoxide, ferrophosphor and slags.

In the field of nitrogen fertilizers, work should be continued on the all-round improvement of the physical properties of ammonium nitrate in order to reduce further its tendency to cake — its hygrocropicity — and to remove its tendency to increase in volume with higher temperatures, and to obtain a granular product. With this aim it is desirable to intensify the analysis of the physico-chemical properties of different modifications of nitrate of ammonia and the influence of various additives, moisture, tempering (rapid cooling) and other treatments. It will be useful to examine from the technical and economic viewpoints the question of the future synthesis of urea from ammonia and and carbon dioxide under Central Asian conditions for use as a high percentage fertilizer and important technical products.

With the aim of preparing high-grade and chlorine-free potassium fertilizers (the latter for some agricultural crops), it is expedient that methods of production of potassium sulfate, potassium nitrate and potassium phosphate on a pilot-plant scale should be mastered. It will be necessary to carry out a number of supplementary physico-chemical investigations of the equilibrium systems and reaction kinetics of the processes occurring when phosphates are decomposed by acids, and also in the processes of baking and fusing them with alkaline compounds and with aluminium silicates. The possibility should be examined of using local resources for gypsum (and further possibly for phospho-gypsum) for the improvement of saline soils and the use of organic substances to improve their structure.

Attention should also be given to the agro technical and economic study of conditions for the application of mineral fertilizers (phosphates, ammonium and nitrate salts, triple fertilizers) in the liquid state, which have been successfully tested by NIUIF in field experiments on northern soils as suggested by Britske [13].

* * *

The research and experimental work enumerated above could not possibly be carried out if the solution of these problems was entrusted to only one institute or one Academy of Sciences, even with a large number of highly qualified workers. Only by planned collaborative team-work, based on a clear division of the work, and in addition with cooperation and mutual aid between the workers in science and industry, will it be possible to solve the problems presented here.

Today we may note with pleasure that in this great work, together with institutes, laboratories, experimental stations of the All-Union and Republican Academies of Sciences, in recent years factories and collective farms have cooperated. We note with pleasure that in recent years steps have been taken to found a fertilizer laboratory in the Uzbekh Academy of Sciences, that already a number of experimental stations are working in Central Asia in the field of agricultural chemistry and in this work practically all the fertilizer factories of Central Asia take part. I hope that the reading of the present paper will help to set forth the most important themes, will aid in their critical selection and will bring together the creative forces for their fulfilment.

In closing I should like to mention that the reading of this report at a combined session of the Uzbekh Academy of Sciences and the Division of Chemical Sciences of the Academy of Sciences USSR was not the result of an attempt to meet local requests of our Uzbekh comrades, but is the result of deeper and weightier considerations. These are based on the fact that it is just in Central Asia and Southern Kazakhstan that the business of producing and applying fertilizers must be devoloped both qualitatively and quantitatively at a high scientific level; because here the the natural resources of power and raw materials are large, and fertilizers are both effective and are needed in large quantities. It is natural, therefore, that this problem should attract not only Central Asian but also all Soviet chemists, agronomists, engineers, who on the basis of Stalin 's tradition of friendship of the peoples, unity of theory and practice, using the growing interrelationship between chemistry and biology, wish to see the best and most progressive and mosteconomical fertilizer production methods and their wide application in agriculture.
If the Central Asian agricultural industry has reached the first place in the world for cotton productivity, then we

wish to see it going forward with all other crops on the basis of a wide utilization of chemical methods in agriculture, and the application of leading methods of agro-technique, irrigation, and the latest achievements of scientific organization in agricultural production.

For, according to the Directives of the 19th Party Congress, the fulfilment of the 5th Five-Year Plan will be one of the greatest steps forward on the road to development from Socialism to Communism. In his outstanding work on economic problems of socialism in the USSR , Comrade Stalin points out that according to the basic economic law of socialism, provision for the maxiumum satisfaction of the constantly growing material and cultural requirements of all society must be effected by the continuous growth and improvement of socialist production on the basis of efficient techniques.

It is useful to remember that the mineral fertilizer industry is one of the largest branches of the chemical industry. The world production of fertilizers at present amounts to more than 35 million tons per year. It continues to grow rapidly both qualitatively and quantitatively. Its growing importance for our country needs no proofs. Naturally, this branch of chemical industry must be developed in the Soviet Union on the basis of the latest achievements in science and technology. I should like to express my confidence that Soviet chemists in close cooperation with biologists and workers in the chemical and agricultural industries will fulfill with honor the Directives of the 19th Party Congress and in this way make their small contribution to the work of building a communist society.

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RECENT DEVELOPMENTS IN THE PHYSICO-CHEMICAL INVESTIGATION OF COTTON FIBER*

K. H. Usmanov

In the discussions of the 19th Party Congress and its Directives on the Five-Year Plan, great attention was devoted to the further development of cotton growing in the USSR. A considerable proportion of cotton is already beginning to come from new cotton-growing regions. The level of production of the cotton plant in the Soviet Union greatly exceeds that of capitalist countries. Last year the amount of cotton fiber worked represented a great increase over that of pre-war 1940. In 1955, the production of raw cotton in the USSR will exceed 1950 by 55-65%.

As a result of the introduction of new varieties of cotton and improvements in the technique of their cultivation, the quality of the fiber has been improved with regard to length, strength, and variety. Soviet cotton is the best in the world. However, we must continually strive to increase the quality of cotton, to improve the varieties with regard to harvesting, and to increase the boll size. There is no doubt that this huge project of the Five-Year Plan for the improvement of the production of cotton and cotton fiber will be fulfilled. The mechanization of agricultural work is developing rapidly, and the science of cotton growing makes it possible to gather from both new and already familiar fields additional millions of tons of high quality cotton fiber.

In view of this huge scale of production of cotton fiber and the large future development which is promised, scientific research institutes devoted to the cotton plant and to cotton fiber must consider two large problems. First, improvement of the quality of cotton fiber by means of selection. Second, the discovery of more rational ways of utilizing different varieties by making a detailed study of the properties of these varieties. It is natural that these problems and their many component parts are being worked out by a great army of Soviet investigators, and already great successes have been attained.

In the present report, our aim is to explain a new proposal in the development of these two problems. This proposal is concerned with the development of new requirements for cotton fiber. It is proposed that additional chemical, or strictly physico-chemical requirements should be instituted for cotton fiber. It is well known, for example, that the fatty and waxy constituents of cotton fiber have a great influence on the preliminary treatment of the fiber and on its spinning; and also that in the finishing of cloth before dyeing, the most difficult particles to wash out of the cloth are the natural impurities in the fiber, natural congeners of cellulose. The content of these impurities, or strictly speaking, the chemical composition of different fibers, as we know, is different for different varieties of the cotton plant.

The chemical composition, for example the content of fatty and waxy substances, plays an essential role in the preparation of special materials such as cord for automobile and aeroplane tires. The quality of the latter is highly dependent on the moisture content of these cords.

The durability of articles prepared from cottonfiber naturally depends almost entirely on the technological properties of the original fiber. In the preaparation of high quality articles, it is necessary to use fibers possessing specific characteristics. The industrial treatment also depends upon these properties. It is quite obvious that a knowledge of only the final or original properties of the fiber is insufficient. It is necessary to know the properties of the fiber under all the conditions of its utilization, and to know how these properties change under different conditions.

All this clearly shows that the time has come to institute for fiber, in addition to the existing requirements for length, fineness, and strength, further physico-chemical standards. In other words, in the introduction of a new variety, the selector must take into consideration not only the yield and the essential qualities enumerated above, (length, fineness, and strength), but also of the chemically valuable properties of the future fiber, and select chemically useful varieties from which to breed. Furthermore, when a given variety of fiber is used in the manufacture of certain articles, the technologist must know the physical, chemical, and mechanical characteristics of this fiber, not only in its original condition, but also under the conditions in which it will be used.

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Only in this way will it be possible to make a rational selection of the method of treatment and to guarantee the preparation of cotton articles having the required qualities. In order to develop these new, as we have termed them, physico-chemical requirments and to relate them to the technological treatment of fiber, team-work by chemists, especially by chemists working in the extensive field of high-molecular-weight compounds, selectors and technologists is necessary. It is necessary to have theoretical and practical cooperation between these and many other related disciplines dealing with cotton fiber, with cellulose, with artificial cellulose fibers and even with cellulose ethers. Work connected with these problems has been, and is being, carried out in many research institutes and laboratories of the Union.

The Uzbekh SSR is one of the most favorable regions for the cultivation of cotton in the Union. It is therefore reasonable to develop the work on the investigation of the cotton plant, including the work on the physico-chemical investigation of cotton fiber, here, in Uzbekistan.

The carrying out of such investigations in our Republic is facilitated by the proximity of selection stations and the possibility of close co-operation between our workers and workers in these stations, as well as in the many institutes in Tashkent working on cotton fiber.

The work of Surova and Zakoshchikov, Ivanova and Kurennova, Rytikov, Korzheniovsky, and Marchenko, in this field carried out 20 years ago was also done in Uzbekhistan [1]. After this work, which embraced a few selection varieties, no serious systematic chemical investigations were carried out on cotton fiber.

Our comparative studies on natural cellulose (cotton fiber) and on hydrated cellulose carried out in 1946 to 1950 in co-operation with Kargin, the basic results of which we reported to the 7th Conference on the Chemistry and Physical Chemistry of High Molecular Weight Compounds in Moscow in June 1952, is the basis of the present work. This threw additional light on the properties of chain-like cellulose macromolecules and made it possible to suggest that "cellulose is a loosely packed material, which results from the great rigidity of the cellulose chains and the difficulty of displacing them. This corresponds with its high elastic properties and its great sorptive power for water. Under any conditions which decrease rigidity and increase the mobility of the cellulose chains, the packing becomes more dense, and this results in a reduced sorption of water. These transitions are of a continuous nature" [2].

We studied the chemical composition, the degree of polymerization and the sorption of fiber at various periods of vegetation and we determined the breaking strength and also recorded deformation curves under different humidity conditions. The same fiber samples were examined in the Institute of Agriculture of the Academy of Sciences, Uzbek SSR before being subjected to several standard industrial tests. The electrical properties of the fibers and of the raw material were studied in the Physical Technical Institute of the Academy of Sciencs, Uzbek SSR mainly with the object of establishing the theory of hygrometers. For these tests, previously labelled pods from the first positions of 2-3 sympodia were collected every five days. After the necessary cleaning, the fiber was examined chemically.

Many workers have been interested in the composition of cotton fiber from different selection varieties. According to a number of investigators, the chemical examination of cotton fiber from different selection varieties, when all the samples are fully matured, does not disclose any difference in the chenical composition which might be utilized to characterize one fiber or another. On the other hand, it has been shown for six American varieties of mature fiber that significant differences are found in the chemical composition of different varieties (cellulose, reducing sugar, wax, etc.) Such contradictory reports are numerous in the literature.

The aim of the present work was to investigate the rate of change in the proportion of cellulose to other materials and yields of cellulose from different varieties of cotton plant according to the vegetation period. Chemical analysis was, for the present, confined to the determination of the main components of the fiber, in order to compare varieties and to measure the rate in change of the content of cellulose, fats and waxes, pectin substances, pentosans, reducing substances, and ash. There are several methods in the literature for the determination of cellulose in the fiber of the cotton plant (Cross-Bevan, Müller, Shalbe-Robinov) [1]. We used the method of Corey and Gray [1] which is different from the method of Shalbe-Robinov in that there is no bleaching, and it is therefore less drastic than the Shalbe-Robinov method. As has been confirmed in the literature, cellulose obtained by the Corey and Gray method may be used for the most precise scientific investigations.

Pectin substances were determined by a modified Viktorov method in the form of calcium pectate [4]. The pentosans were determined by the method of Tollens by treating the fiber with 12% hydrochloric acid, distilling off the furfural formed and precipitating it with phloroglucinol [5]. For the determination of reducing sugars, a weighed sample of fiber was treated with distilled water and boiled under a reflux condenser for four hours; the reducing substances were then determined in the extract by the method of Issekuts. The ash was de-

determined by igniting the fiber to constant weight in a porcelain crucible at [illegible]°.

In all the determinations allowance was made for the relative humidity of the laboratory air. The content of moisture in the fiber was determined from the relative humidity and the [illegible], and the absolute dry weight of sample calculated. The results of all the analyses are based on this absolute dry weight. Some results of the mechanical investigations of seven selection varieties are shown (Figs. 1-5).

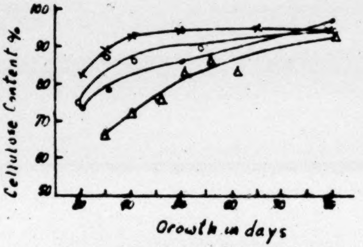

Fig. 1. Dependence of cellulose content in different varieties of cotton, on ripeness: △ — 1306 DB ● — S-450-555; o — 18819; × — 3210.

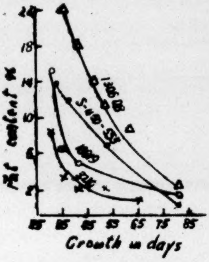

Fig. 2. Dependence of fat and wax content in different varieties of cotton, on ripeness.

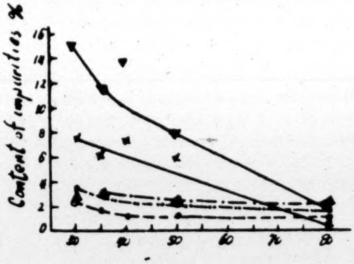

Fig. 3. Dependence of impurities content in fiber of varieties S-450-555, on ripeness; [illegible] — [illegible]; x — reducing sugars; ∨ — fat and wax.

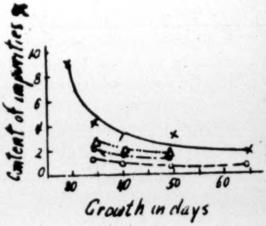

Fig. 4. Dependence of impurities content in fiber of variety 3210, on [illegible]; ● — ash; △ — pentosans; × — fat and wax.

From Figure 1 it is clear that for the same growth of fiber different varieties of cotton have different cellulose contents, this discrepancy becoming smaller toward the end of vegetation, but not falling to zero. Eighty-day fibers of different sorts also differ from one another in their cellulose content. The growth of cellulose in all varieties is significant at the beginning of vegetation and slows down toward its end. In most of the varieties 85-90% of the total accumulated cellulose is built up in 40 days of the vegetation period, the further accumulation being at a slower rate.

There are two characteristic differences in the accumulation of cellulose between different varieties. In variety 3210 after 40 days, 90% of the cellulose had been accumulated, but in variety 108-F, 107-F, S-460 and others, only 80 to 85% of the cellulose had been accumulated in this period. [illegible] this difference in growth of the amount of cellulose depends also upon the agricultural, technical and other conditions under which the plant is grown; but the influence of variety is clear. It appears to us that this difference is connected with the period of maturing of the cotton plant and it is possible indirectly to predict the date of opening of the pods 30 to 40 days ahead. This connection between variety and chemical composition evidently exists not only in relation to the accumulation of cellulose, but is also shown by the other components of the fiber. For example, by the relative decrease in the fatty and wax components of the fiber,* which is evident from Figure 2, where the greatest rate of change occurs with variety 3210.

The other figures show changes in different impurities of the cellulose with ripeness of fiber for three

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* In our experiments the fatty and wax fraction is defined as the total loss in weight on ethanol-ether extraction.

TABLE

Growth of cotton in days	Cellulose viscosity in centipoises			
	Fuadi	Maarad	No. 0491	No. 246
30	1080	652	1058	1377
45	2557	1194	1142	2036
70	3550	1316	2243	3028

selection varieties of the 1951 harvest. From these figures it is clear that a marked fall in the content of pectin substances, pentosans, and ash in all varieties concludes at the 35th to 40th day. Up to the 60th day from the day of flowering the content of these substances in the fibers is within the limit 1 - 2% but varies with different varieties. In 25 - day growth the content of these substances reaches 4%.

As will be seen from these graphs, each variety of cotton plant has its own kinetics of fiber development, that is the kinetics of change in the chemical composition of the fiber in the vegetation period.

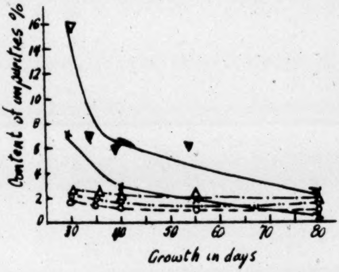

Fig. 5. Dependence of impurities content in fiber of variety 18819, depending on growth: o −pectins; ● −ash; △ −pentosans; ✕ −reducing sugars; ▼ −fats and wax.

Samples of purified cellulose obtained by the method of Corey and Grey were used to determine the degree of polymerization. It is known that the main reactions in the formation of high polymers are polymerization and polymer condensation, and as a result of these the long molecular chain is produced. The bio-chemical synthesis of cellulose, which has not been fully elucidated, proceeds by one of these reactions. If we assume that the biochemical synthesis is due to polymerization, then the molecular weight of the cellulose in the process of fiber growth should not change. On the other hand, if the process is one of condensation, the molecular weight of the cellulose should change with the growth of the fiber. Therefore, in the elucidation of this problem, determination of the molecular weight of cellulose during the process of vegetation of the fiber is one of the main methods; and this process is important in the chemistry of the cotton plant.

That the maturing of the fiber is a process in which cellulose is accumulated has been confirmed by the results of chemical analyses carried out previously by Ivanova and Kurennova. They showed that the amount of cellulose deposited in the walls of the cotton fiber changes with the ripening of the pod [1]. Surova has observed that the degree of polymerization of four varieties of cotton increases as the fiber matures. Moreover, for one and the same degree of maturity of fiber, differences were observed in the viscosity of the cotton fiber cellulose for different selection varieties of cotton (see table).

The concept of the maturity of cotton, which is always identified with the opening of the pods, is in actuality more complicated. The moment of opening of the bolls, considered as the sign of the end of ripening of all its elements, in the case of cotton may not coincide with complete deposition of cellulose in the fiber; on the contrary, the deposition of cellulose may precede opening of the pods. Thus, it is necessary to distinguish maturity of the bolls from maturity of the fiber.

There is some data in the literature which indicate that the molecular weight of the cellulose increases with the growth of the fibers. Therefore, if the rate of change of the molecular weight over the period of vegetation were systematically followed, it would be possible to determine how the molecular weight depended on time, and this would make it possible to relate the molecular weight to the degree of maturity of the cotton fiber.

Moreover, a large difference in the properties of cotton fiber of different varieties and of different degrees of maturity and growing under different climatic and agronomical conditions would be determined by differences in their molecular weights; and here the determination of the relationship should be carried out. The establishment of the laws of change in the degree of polymerization of cellulose of different varieties in the vegetation period would enable problems on the rate of maturing of the cotton plant to be explained by the conditions of biochemical synthesis of cellulose.

In our experiments the degree of polymerization was determined by the viscosity method in an Ubbelohde apparatus under the pressure of pure nitrogen, the precautions with regard to oxygen pointed out in the papers of Golova and Ivanov, Shults, Guzeman, Dzhoiner and others [6], being taken.

The results of the experiments are shown in Figures 6 and 7. As will be seen, results of measurements made in 1951 are different from the results obtained in 1952 on the same samples, which had been kept under laboratory conditions for about a year.

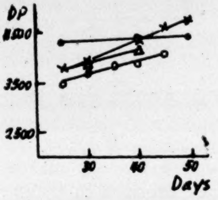

Fig. 6. Degree of polymerization for samples: −×−460; ● − S−3210; Δ −137 −F; o −108 −F

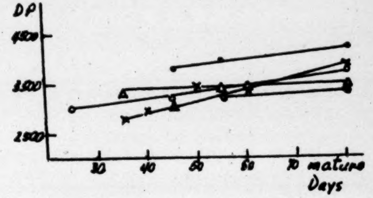

Fig. 7. Degree of polymerization for samples: ● −18819; o −450-555; ● 108 - F × − 1306−DB ; Δ − S -3210.

Values for the degree of polymerization determined on cotton cellulose after it had been stored for a year were much lower than those obtained initially. Evidently, atmospheric conditions and duration of storage have some influence on the degradation of cellulose.

Moreover, in these two series there are some figures which do not support the general tendency of the remaining ones. This evidently must be regarded as a weakness in our experiment and generally in the method of determining the molecular weights of polymers, but a careful analysis of the results clearly shows the presence of definite relationships in the change of molecular weight of cellulose in the samples we have studied.

In all the samples we examined, an increase in the degree of cellulose polymerization as the fiber matured was observed. For the same growth period, the increase in molecular weight differed with different varities of cotton; in other words, the law governing the growth of the degree of polymerization is different for different selection varieties. In the same way the magnitude of the degree of polymerization also differs. Variety 3210 as is known, is the most rapidly maturing of all the samples we examined, but as will be seen from the results given, the magnitude of the degree of polymerization remains practically unchanged with growth. It is probable that for the rapidly maturing varieties the degree of polymerization quickly reaches the normal value in the early stages of development of the fiber and, therefore, remains constant during the further growth of the fiber. Therefore, for unripe growths a constant molecular weight after 25 to 30 days growth, with a relatively high absolute value, is evidence of the rapid maturing of the given selection variety of the cotton plant.

As well as determining the degree of polymerization of the cellulose, we determined the hydrogen ion concentration of the sap from the cotton pods of a 25 - day old growth of variety 108 - F. The determination was carried out by two methods: the electrometric and the indicator method.

In the first case we used both the hydrogen and the quinhydrone electrodes. In determinations with the hydrogen electrode the pH was 6.1 and with the quinhydrone, 6.8 - 6.6. The determination by the indicator method gave a value of pH 6.0 - 6.1. From the results obtained it may be assumed that the value was pH 6.0 - 6.1, i.e. the development of the fiber takes place in a weakly acid medium.

The sorption studies and the mechanical behavior examination were carried out on cotton fiber freed from impurities. The sorption was determined by the method of the vacuum sorption balance with a sensitive quartz barrel in a thermostat. The water for the sorption and the samples of cotton fiber were carefully degassed before the sorption isotherm was recorded [2]. The results of the sorption measurements are given in Figures 8, 9 and 10.

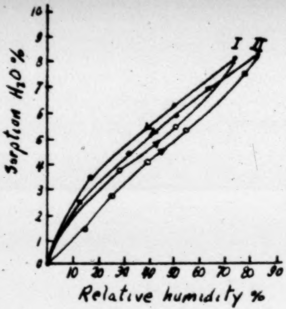

Fig. 8. Sorption and desorption of water on cellulose of 65-day and 25-day cotton, variety 3210, at 25°; o – sorption; ● – desorption; (I) 25-day; (II) 65-day.

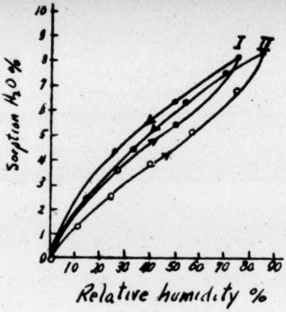

Fig. 9. Sorption and desorption of water on cellulose of mature and 25-day cotton variety 18819, at 25°; o – sorption; ● – desorption; (I) 25-day; (II) mature.

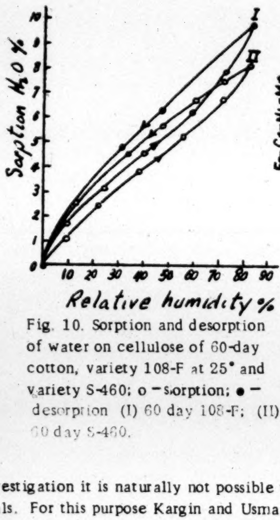

Fig. 10. Sorption and desorption of water on cellulose of 60-day cotton, variety 108-F at 25° and variety S-460; o – sorption; ● – desorption (I) 60 day 108-F; (II) 60 day S-460.

Fe-Cr-Ni-Mn

In all the sorption experiments the establishment of sorption equilibrium was confirmed by recording the sorption kinetics. Complete equilibrium was established after a few hours, or after days. Experiments carried out with fiber and with cotton wool without preliminary removal of air from the sorption apparatus gave slow kinetics of sorption, evidently because of "air pockets", and retarded diffusion at the phase boundaries. On the basis of a series of similar experiments carried out in connection with the Republican Conference on Cotton Driers organized by the Academy of Sciences, Uzbekh SSR, the advantages of the layer type of drier construction proposed by the Energetics Institute of the Academy of Sciences, Uzbekh SSR, were shown.

Our investigations on fiber mechanics were devoted to a study of the mechanical properties (deformation and breaking load) of cotton cellulose in relation to humidity, variety, and time of vegetation. In order to obtain trustworthy dynamometric results, it is necessary to use completely purified cellulose preparations from which all impurities have been removed, especially traces of moisture, since traces of the latter have a powerful influence, and affect the physico-mechanical properties of the material. In such an investigation it is naturally not possible to use existing dynamometers which are intended for testing fibrous materials. For this purpose Kargin and Usmanov have constructed a special electric vacuum dynamometer which permits the examination of fiber under any given humidity condition, as well as in a completely dry state, under a high vacuum [2].

Thus in this work we first studied the relationship between the mechanical properties of cotton fiber and its humidity over a wide humidity range. We examined samples of varieties 3210, 18819, and S-460 at different vegetation periods. For every vegetation period, experiments were carried out on the dry fiber and also at relative humidities of 15, 38, 60 and 85%.

Figures 11 and 12 give deformation curves for absolutely dry and moist fiber, variety 3210, of 35- and 45-day growth, depending on load. As will be seen from the curves, absolutely dry fiber has almost a straight-line deformation up to the breaking point. Such a fiber undergoes only slight extension on breaking, and corresponds to the glasslike state of cellulose, but the presence of an appreciable deformation in completely dry cellulose is evidence of the loose packing of this substance in the glass-like state.

The considerable deformation suffered by fiber in the moist condition may evidently be explained in two ways: [1] by the plasticizing effect of moisture on the fibre with a change in the intermolecular forces; and [2] by a change in the flexibility of the cellulose chains. The mechanism governing the increase in deformation with the increased moisture might usefully be the subject of a discussion. As has been said above, cellulose chains are rigid, and this chain rigidity should lead to the minimum deformation of rigid polymers. It also determines the presence of loose packing, since from rigid rods - if we roughly imagine the molecular model in the amorphous state - it would be possible to obtain densely packed material. This results in the presence of much deformation, even in the absolutely dry state, and the large sorption capacity of cellulose materials, as well as the high rate of diffusion of gases and vapors through them [9].

Consequently, from our work on the mechanical behavior of cellulose fibers carried out over a wide range of moisture content, the conclusion may be drawn, and this evidently is also applicable to polymers with rigid chains, that for this class of polymer a secondary deformation mechanism operates, though for flexible rubber-like polymers the deformation is determined only by the great flexibility of the chains (for crystalline polymers by the remelting of the crystals). For rigid cellulose- like polymers the deformation is determined by the flexibility and by the presence of loose packing. The deformation process of rigid polymers consists of two mechanisms. The elastic component is evidently determined mainly by the loose packing, and the highly elastic component by the flexibility of the chains. As to the explanation for the effect of moisture on the increase in deformation, as has been shown, our experiments carried out in co-operation with Kargin have demonstrated that water changes the density of cellulose packing only at high temperatures (200°). Therefore water mainly acts through its effect on the flexibility of the chains, and by its plasticizing action.

The variations in the mechanical properties of several varieties of cotton cellulose with moisture content at 20° is shown in Figures 13, 14, and 15. Each point on the diagram represents the mean deformation and load value obtained from 100 to 120 individual measurements.

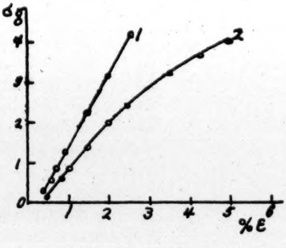

Fig. 11. Deformation of 35-day cotton fiber, variety 3210, depending on load. 1) Absolutely dry fiber; 2) fiber at 85% humidity.

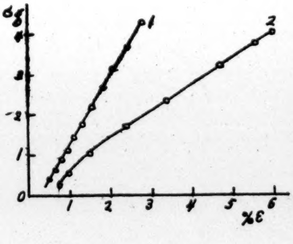

Fig. 12 Deformation of 45-day cotton fiber, variety 3210, depending on load. 1) Absolutely dry fiber; 2) fiber at 85% humidity.

These curves show that there is a fairly strong relationship between the mechanical properties and vegetation period of cotton fiber. Indeed, as the pod ripens, as well as an increase in the breaking load, there is also observed an increase in the deformation. The increase in the deformation with the fiber age is evidently caused by a thickening, that is by the deposition of cellulose in the fiber. It is of interest to note that in sample 3210 the breaking load, that is its strength in comparison with other varieties, increases only slightly with the degreee of maturing of the fiber. Thus, for example, the breaking load of absolutely dry 35-day fiber is equal to 4.2 grams and of 55-day, 4.5 grams. Evidently this is connected with the fact that variety 3210 is a more rapidly maturing type than the others which we have investigated. Evidently, the deposition of cellulose takes place rapidly and the fiber strength reaches a maximumvalue at an early period of growth, and changes only slightly during the remainder of the vegetation period. As will be seen from the results given, the presence of moisture in cellulose fiber considerably changes its mechanical behavior picture, an increase in moisture causing a fairly smooth and notable increase in its breaking strength and a more marked increase in its length. In contrast to natural fibers, artificial fibers in the moist state, as is known, not only do not increase in strength but, on the contrary, suffer a reduction of 50 - 60%. This difference in the behavior of natural and artificial fibers may evidently be explained by the fact that cotton fiber in its nature is strongly oriented and possesses in comparison with viscose rayon some degree of polydispersion, and also spirally disposed chains. It consists of the largest types of macromolecules, not differing greatly among themselves in molecular weight, unlike artificial fibers. This difference confers on cotton fibers exclusive properties, including its power of increasing in strength with increased moisture content. As regards the lengthening of fiber with increase in moisture content, with an initial increase in the moisture content of absolutely dry cellulose there is a slight increase in length; with a further increase in the moisture content of the fiber, within the moisture limits of 4.0 - 6.0% there is a marked increase, which is followed by a slowing down.

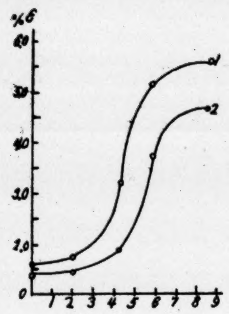

Fig. 13. Relation between the deformation of cotton cellulose, variety 3210, with the moisture, for different vegetation periods: (1) 35-day cellulose; (2) 45-day cellulose.

Thus the deformation-moisture graph for cotton fiber is S-shaped, similar to the type previously obtained for viscose rayon [7]. These two types of cellulose have this in common; the region of rapid growth in the deformation corresponds to the same relative moisture content.

If we compare our results with those of Mikhailov and Kargin [8] on the flow of highly swollen cellulose fiber, then we obtain a picture which has a great similarity, at least in its external form, to the well-studied picture of the deformation change with temperature under different time conditions. In fact, whereas in the experiments of Mikhailov and Kargin on highly swollen (wet) fibers the viscous state of flow was reached, in our experiments over a wide range of moisture content, limits were indicated for the appearance under the given time conditions (the deformation limit was reached in 2 minutes) of highly elastic and glasslike states of cellulose; this elastic state of the fiber appears at a much lower temperature than vitrification which, as is known, takes place at a higher temperature, about that which cellulose decomposes. Consequently, the water absorbed by cellulose under ordinary atmospheric conditions changes it from the glasslike state and, as a result makes possible the appearance of those highly elastic properties at normal temperatures which are so valuable in the technology of textile threads.

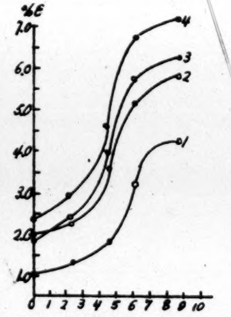

Fig. 14. Relation between the deformation of cotton cellulose, variety 18819, with the mositure at different vegetation periods. 1) 30-Day cellulose; 2) 40-day cellulose; 3) 50-day cellulose; 4) mature cellulose.

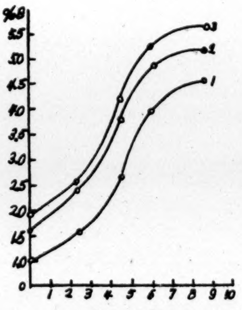

Fig. 15. Relation between the deformation of cotton cellulose, variety S-460 with the moisture, for different vegetation periods. 1) 35-Day cellulose; 2) 45-day cellulose; 3) 60 day cellulose.

The presence of moisture in fiber thus has a powerful effect on the deformation processes, and for this reason, in describing the mechanical properties of cellulose materials, it is necessary to take account of the conditions under which they will be used. Here also may be put forward an hypothesis of a correlation between the character of the mechanical-properties curve of the fiber of different varieties and the rate of maturing of these varieties. In fact, the outstanding characteristic of the curve representing the change in strength of fiber, variety 3210, with age points to its rapidity of maturing.

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THE AUTOXIDATION OF ALLO-OCIMENE AND THE INTERMEDIATE PRODUCTS FORMED IN THE AUTOXIDATION PROCESS

G. L. Dranishnikov

The autoxidation processes and intermediate products which have been most studied up to the present time are those dealing with the autoxidation of paraffin, cyclo-olefinic and aromatic hydrocarbons, and their derivatives [1]. On the other hand, the autoxidation processes and products of unsaturated aliphatic hydrocarbons have practically not been investigated at all up to now. Only in the case of the simplest olefins, for example, n-hexene, have detailed studies of the autoxidation products been made [2]. The more complicated olefinic hydrocarbons, including the dienes and trienes, which are of considerable practical interest, have not been subjected to detailed investigation, although the need for such investigation is very obvious.

In the course of work on the preparation of some derivatives of one of the aliphatic terpenes, allo-ocimene (2,6-dimethyloctatriene-2,4,6), we were impressed by the extreme ease of autoxidation of this hydrocarbon, and we resolved to study the process and the autoxidation products in greater detail. The marked tendency of allo-ocimene to autoxidize was first noted by B. A. Arbuzov [3], who established that the product formed had a composition closely corresponding to $C_{10}H_{16}O_2$, and gave a positive reaction for peroxides with potassium iodide.

Nikitin [4] studied the end-products obtained by the vacuum distillation of highly oxidized allo-ocimene, and he concluded that as a result of this treatment two products were formed: one was an unsaturated monohydric terpene alcohol (allo-ocimenyl alcohol), of composition $C_{10}H_{16}O$, obtained in a yield of about 50%, and the other consisted of a residue of solid polymer, the structure of which was not established. Apart from a small quantity of unreacted allo-ocimene and dipentene, present as impurity, no other products were observed. These studies contain the only information available on the autoxidation products of allo-ocimene. The mechanism of the process and the intermediate products have not been studied at all.

Allo-ocimene is a highly unsaturated aliphatic hydrocarbon with three conjugated double bonds in its molecule, which confer on it a high degree of chemical reactivity. There is no doubt that the extreme ease of oxidation of this hydrocarbon is determined by its highly unsaturated character, and the characteristic orientation of the double bonds in its molecule; these also have an influence on the direction of oxidation, and on the secondary reactions of the initially formed autoxidation products. The autoxidation of allo-ocimene shows considerable differences from the autoxidation of paraffins and simple alkene hydrocarbons, both in regard to the course of the reaction and to the primary and secondary products; this is proved in a conclusive manner by the experimental results given here.

The oxidation of allo-ocimene was effected in two ways: by allowing it to stand at room temperature for a time exposed to the air in vessels protected from dust, or by bubbling either air or pure oxygen through the liquid contained in tall, narrow vessels. The rate of absorption of oxygen at different stages in the autoxidation process was studied by means of the apparatus described by Zelinsky and Borisov [5].

Experiments showed that the allo-ocimene autoxidation process proceeds in a very characteristic manner, and several distinct stages in the process can be distinguished, not only by external criteria, but also by the chemical properties of the intermediates produced in the different stages. A study of the nature of these main intermediates and their interconversion, as well as the kinetics of the process, now enables us to draw some conclusions as to the nature of the allo-ocimene autoxidation process. These conclusions and observations may be of interest not only in the study of allo-ocimene, but also in the investigation of other aliphatic hydrocarbons having several conjugated double bonds.

In the present paper we shall describe the course of the allo-ocimene autoxidation process, and we shall give the chemical properties of the intermediates formed in the principal stages of this process.

In the first stage of the process, molecular oxygen vigorously combines with the allo-ocimene and extensive polymerization takes place. When one molecule of oxygen has been added to the allo-ocimene, exposed in a thin layer, it is converted to an unstable polymeric peroxide compound — a polyperoxide of the composition $(C_{10}H_{16}O_2)n$, consisting of a spongy, elastic mass. After this vigorous absorption of one molecule of oxygen, further combination with oxygen and formation of polyperoxide is completely stopped for some time. Thus, the first stage in the autoxidation results in the formation of a polyperoxide, and this may be termed the oxidative-polymerization stage; it may be represented as follows:

$$\underset{\text{Allo-ocimene}}{nC_{10}H_{16}} + nO_2 \longrightarrow \underset{\text{Allo-ocimene polyperoxide}}{(C_{10}H_{16}O_2)n}$$

The peroxide nature of the main product of the first stage of autoxidation (the polyperoxide) is confirmed by the reaction of this product with potassium iodide, iodine being liberated, and also by its color reactions with guaiacum and with thiocyanate [1]. The polyperoxide does not react with lead tetraacetate and concentrated alkali solutions, which suggests that it does not contain appreciable quantities of hydroperoxide oxygen.

It is probable that the polyperoxide has a structure of the dialkyl peroxide type. It is poorly soluble in the usual organic solvents (and this property may be utilized in removing possible impurities), and is unsaturated: the degree of unsaturation was found to correspond to about two double bonds for each elementary molecule $C_{10}H_{16}O_2$. Because of its poor solubility and its instability, we were unable to determine its molecular weight.

The polyperoxide is very unstable, and decomposes on standing, or still more rapidly when slightly heated. When stored it lasts for only a few days. When sealed in ampoules without access of air, the polyperoxide is completely converted to a liquid in 7 to 10 days. This is the result of spontaneous depolymerization with the formation of the monomeric polyperoxide, $C_{10}H_{16}O_2$.

The slow conversion of the polyperoxide to the monomer is the second main stage in the allo-ocimene autoxidation process, and we term it the autodepolymerization stage. In this second stage there is no addition of oxygen. Only spontaneous depolymerization of the polyperoxide takes place. This was proved both by experiments in which the polyperoxide was stored in sealed ampoules, and also by a study of the oxygen absorption curves obtained when allo-ocimene was oxidized in the apparatus described above.

The polyperoxide depolymerization process proceeds at a rapid rate, and on heating to 60-70° for a short period it becomes strongly exothermic. The temperature then rises spontaneously to 165-175°, and the whole of the polyperoxide is converted to a liquid monomer having an elementary composition very close to that of the polyperoxide; this monomer is identical in chemical properties with the monomer formed by the slow spontaneous depolymerization of the polyperoxide.

The second main stage in the allo-ocimene autoxidation process may be represented as follows

$$\underset{\text{Polyperoxide}}{(C_{10}H_{16}O_2)n} \xrightarrow{\text{Autodepolymerization}} \underset{\text{Secondary oxide}}{nC_{10}H_{16}O_2}$$

Vacuum distillation of the products of both the spontaneous and thermal depolymerizations established that both these products consist of the same single monomeric component having the composition $C_{10}H_{16}O_2$; we term this the secondary oxide.

The purest sample of secondary oxide which we obtained was an almost colorless, mobile liquid with a characteristic odor, and having the following constants: b.p. 84-84.5° at 4 mm; n_D^{20} 1.4630-1.4635; d_4^{20} 0.951; M 168. The elementary composition was $C_{10}H_{16}O_2$, with one double bond.

Unlike the polyperoxide, the secondary oxide is not a peroxide compound, but, as our investigations showed, an aliphatic unsaturated terpene α-dioxide.

On hydration the secondary oxide forms the corresponding aliphatic unsaturated terpene tetrahydric alcohol — tetrite — in good yield; this has the composition $C_{10}H_{20}O_4$, and m.p. 124-125°.

Interaction of the secondary oxide with methanol in the presence of traces of sulfuric acid gave the dihydroxydimethyl ether, $C_{12}H_{24}O_4$, containing two hydroxyl and two methoxyl groups in the molecule (the constants of this ether are given in the experimental section).

When the secondary oxide was catalytically hydrogenated on a skeletonized nickel catalyst at ordinary pressure and room temperature, it took up 3 molecules of hydrogen per molecule to form a saturated aliphatic glycol of the terpene series, $C_{10}H_{22}O_2$ (the constants of this glycol are also given in the experimental section). These results provide sufficient confirmation that the secondary oxide is of the α-oxide type, and that it belongs to the aliphatic terpene series.

When the crude, undistilled products of the thermal or the spontaneous depolymerization of the polyperoxide were hydrated, we obtained in quite satisfactory yields a crystalline tetrite identical with the tetrite obtained by hydration of the pure secondary oxide. This is further proof that the secondary oxide is a normal product of the second stage in the autoxidation of allo-ocimene – the depolymerization stage – and is not formed during the vacuum distillation of the autoxidation products.

Therefore, the thermal and spontaneous depolymerization processes undergone by allo-ocimene polyperoxide are are essentially the same, the only difference being in the reaction rate.

The spontaneous depolymerization of allo-ocimene polyperoxide is an uncommon and very interesting example of the smooth decomposition of an organic peroxide compound to give an almost quantitative yield of dioxide.

If we assume that the polyperoxide has a dialkyl peroxide structure (and this is confirmed by experiment), then the polyperoxide depolymerization process must be considered as a complex of several simultaneous reactions: rupture of the oxygen-oxygen and the ethylene bonds of the polyperoxide with the subsequent closure of the free oxygen and carbon bonds formed to produce an α-oxide ring and a secondary oxide double bond.

The elucidation of the actual depolymerization mechanism depends on the precise determination of the position of the ethylene bond and the oxide rings in the secondary oxide molecule, and we shall presently consider these points. The formation of the secondary oxide concludes the second main stage in the allo-ocimene autoxidation process – the autodepolymerization stage.

In the third stage of the process more molecular oxygen is added to the secondary oxide. Since the secondary oxide is more saturated than the starting allo-ocimene, the rate of oxidation in this stage is several times slower than the rate in the first stage.

We did not succeed in separating any single compound from the products of the third autoxidation stage. These consist of a complex mixture of products, all at different stages of oxidation; and they include oxidation products of the secondary oxide and unreacted secondary oxide, the proportions depending on the length of the oxidation; the unreacted oxide can be separated by vacuum distillation. The residue obtained after distillation of the third stage products consists of a resinous product of variable composition, corresponding, on the average, to the general formula $C_{10}H_{16}O_3$.

From the results obtained, the allo-ocimene autoxidation process may be represented by the following main stages:

$$\underset{\text{Allo-ocimene}}{nC_{10}H_{16} + nO_2} \xrightarrow[\text{polymerization}]{\text{oxidation}} \underset{\text{Polyperoxide}}{(C_{10}H_{16}O_2)n} \xrightarrow{\text{autodepolymerization}} \underset{\text{Secondary oxide}}{nC_{10}H_{16}O_2}$$

EXPERIMENTAL*

Allo-ocimene was prepared by the thermal isomerization of α-pinene according to B. A. Arbuzov's method, [3]. Allo-ocimene with the following constants was used in the reaction: b.p. 81-82° at 12 mm; n_D^{20} 1.5430-1.5440; d_4^{20} 0.810-0.812.

Autoxidation of allo-ocimene

Experiment 1. Freshly distilled allo-ocimene was poured into flat beakers to form layers about 0.5 cm thick. The beakers were loosely covered with glass plates and allowed to stand in diffuse light. After 4 days nearly all the allo-ocimene was converted into a silvery, elastic mass of polyperoxide. An elementary analysis of this crude polyperoxide (the product was separated from a small amount of unoxidized allo-ocimene by squeezing between filter paper) gave the following results:

Found %: C 71.44; H 9.24.
$C_{10}H_{16}O_2$. Calculated %: C 71.42; H 9.53.

Experiment 2. Dry air was bubbled through a solution of freshly distilled allo-ocimene in ethanol (1: 1) in a narrow vessel at room temperature. The bubbler consisted of a tube with a porous glass plate sealed on the end to provide a large contact surface between the allo-ocimene and the air. About three hours after the bubbling had commenced, white flakes of insoluble polyperoxide formed on the bottom of the cylinder. Heat was evolved slowly during the autoxidation process. From time to time the precipitated polyperoxide was removed from the bottom of the cylinder and fresh allo-ocimene was added.

The polyperoxide obtained in this way was washed with ethanol and dried to constant weight in a vacuum desiccator at 30-35°. After drying, the polyperoxide consisted of an almost colorless elastic mass resembling rubber gelled in benzene. The elementary analysis of this polyperoxide was the same as that of the polyperoxide obtained in Experiment 1; both corresponded to the general formula : $C_{10}H_{16}O_2$.

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* With the participation of E. A. Kalinovskaya and L. G. Konchevskaya.

Allo-ocimene polyperoxide is poorly soluble in such organic solvents as dioxane, acetone, ethyl acetate, diethyl ether, chloroform, petroleum ether, and benzene; and it is insoluble in methanol and ethanol. We made use of this property to separate it from allo-ocimene and other possible impurities. The polyperoxide was purified in the following manner: the crude material, obtained by either method, was carefully mixed in a beaker with five times as much ether to give a homogeneous, colloidal-like mass. Absolute ethanol was added to this mass to precipitate the polyperoxide, which separated as white flakes. After the solvent had been decanted, the polyperoxide was washed three times with ethanol and dried in vacuo at 30-35°. It was then obtained in the form of a colorless, elastic, rubber-like mass. Purification caused no material change in the elementary composition.

Investigation of the polyperoxide

1. Nature of the polyperoxide oxygen bonds

When the ethereal suspension of the polyperoxide (the ethyl ether must be freshly distilled) was shaken with aqueous potassium iodide solution, much iodine was liberated, and this reaction was evident even without the use of starch. The suspension also gave an intense blue color with guaiacum in the presence of ferric salts. Both of these reactions prove that the polyperoxide contains peroxide oxygen.

A very characteristic and sensitive reagent for peroxide compounds is the well-known thiocyanate, which consists of an aqueous acetone solution of ferric chloride and potassium thiocyanate. With the aid of this reagent it is possible to detect both organic hydroperoxides, and also the much less reactive dialkyl peroxides [1]. In a test tube 0.1 g of the polyperoxide and 4 ml of thiocyanate were placed. Immediately the original bright yellow reagent changed to dark red in the presence of the polyperoxide.

In order to establish the nature of the peroxide oxygen in the polyperoxide, reactions were carried out with lead tetra-acetate; these, as is known, are very characteristic for peroxide compounds containing hydroperoxide groups, and they proceed with the latter vigorously and with the spontaneous evolution of heat and oxygen [1]. It was found that the polyperoxide does not react with lead tetra-acetate, and from this it may be assumed that it does not contain notable quantities of hydroperoxide oxygen. It is probable that the polyperoxide has a dialkyl peroxide structure. However, this assumption needs further experimental proof, since, according to the method of Terentyev, the polyperoxide was found to contain 0.2% of active hydrogen, the nature of which we have not yet elucidated.

2. Determination of the degree of unsaturation of the polyperoxide

The determination was effected by titrating a weighed sample of polyperoxide in chloroform solution with benzoyl peroxide, according to the method of Nametkin and Bryusov [6]. 0.1926 g substance; 0.1826 g substance was added to 15 ml of benzoyl hydroperoxide solution. After two days, a back titration showed that 18.7 ml; 19.9 ml had been consumed. Found for $C_{10}H_{16}O_2$. 1.35, 1.37

Titration with benzoyl peroxide or hydroperoxides of other acids cannot be considered an accurate method for the determination of unsaturation in a polyperoxide, since the possibility that a further quantity of iodine might be separated, due to the action of the polyperoxide itself, in the process of titration of the excess benzoyl hydroperoxide, cannot be excluded.

The result obtained may be low compared with the true value, the number of double bonds being less. However, since other known methods (bromination, iodination) were found to be entirely unsuitable in our case, we decided to use this method. Bearing all that has been said above in mind, it can definitely be stated that the polyperoxide contains not less than two double bonds per elementary molecule $C_{10}H_{16}O_2$.

3. Behavior of the polyperoxide on storage without access of air (autodepolymerization of the polyperoxide

About 10 to 15 g of the polyperoxide was sieved into a small glass ampoule, air being excluded, and the ampoule was then stored in the dark at room temperature, and examined from time to time to find if the external appearance of the contents had changed. After 2 to 4 days, a gradual liquefaction of the original elastic polyperoxide mass was observed, and after 7 to 8 days the contents of the ampoule had become entirely converted to a mobile, yellow liquid (product of spontaneous depolymerization) with n_D^{20} 1.4850-1.4890. On opening the ampoule, neither diminution or increase of pressure was observed; this confirms that the process of spontaneous depolymerization proceeds without further addition or removal of oxygen. One of the ampoules was opened after 6 months, and the contents were identical with, and had the same constants, as those found after 7 to 8 days.

The depolymerization product, unlike the peroxide, did not give the reactions described above, and was notable for its high sensitivity to acids. The addition of a drop of decinormal mineral acid, or the acid salt of a mineral acid dissolved in water, produced an immediate reaction in which resinification took place with evolution of heat. Anhydrous acid salts and organic acids had no action on the depolymerization product in the cold.

The depolymerization product takes part in reactions characteristic of α-oxides; it reacts in the cold with concentrated aqueous ethanolic solution of manganese chloride, manganese hydroxide being separated with the formation of an oil containing chlorine, and it also gives a brown coloration with an ethanolic solution of pyridine.

On distillation under reduced pressure, the depolymerization product was obtained in the main fraction with b.p. 82 to 84° at 4 mm; n_D^{20} 1.4645, 1.4650; and d_4^{20} 0.951, 0.952, having the composition $C_{10}H_{16}O_2$.

4. Behavior of the polyperoxide on heating (thermal depolymerization of the polyperoxide)

10 g of the purified polyperoxide was placed in a round-bottomed flask connected to a reflux condenser. Inside the flask a thermometer was fixed so that the mercury bulb was immersed in the polyperoxide. The flask was slowly heated on a water bath from 20°. When the temperature of the bath had reached 65°, the polyperoxide began to melt with vigorous decomposition, and the evolution of a large amount of heat, which resulted in a rise in temperature within the flask to 170° (spontaneous). The vigorous decomposition reaction continued for a minute. There was no marked change in the weight of the flask before and after the reaction. As a result of the reaction the polyperoxide was converted into a mobile, bright yellow liquid (with the constants: n_D^{20} 1.4740; d_4^{20} 0.944).

Found %: C 70.6, 70.71; H 9.6, 9.62
$C_{10}H_{16}O_2$. Calculated %: C 71.42; H 9.53.

The thermal depolymerization product, like the autodepolymerization product, reacts vigorously with mineral acids and with aqueous solutions of acid salts in the cold. It resinified with spontaneous evolution of heat; it did not give the qualitative reactions for peroxide; it reacted with manganese chloride, and gave a coloration with pyridine.

On distillation under reduced pressure, the thermal depolymerization product was obtained in the main fraction with b.p. 82-84° at 4 mm; n_D^{20} 1.4650, and d_4^{20} 0.951. The fraction had the elementary composition $C_{10}H_{16}O_2$. The chemical properties of the fraction were entirely analogous to the properties of the fraction obtained when the spontaneous autodepolymerization product of the polyperoxide was distilled.

Further experiments showed that the spontaneous and thermal depolymerization products consisted of one and the same compound, which we have termed the secondary oxide. These depolymerization products and the main fractions obtained by their distillation under reduced pressure did not differ in elementary composition or in chemical properties, and they were also very similar in their physical constants. From this it may be concluded that both the spontaneous and the thermal depolymerization of the polyperoxide are similar to one another.

Investigation of the polyperoxide depolymerization product (secondary oxide)

1. Preparation of pure secondary oxide

The impurities in the secondary oxide may include a small quantity of unreacted allo-ocimene, and also isomerization products of the secondary oxide itself containing carbonyl groups. The secondary oxide was easily purified by repeated distillation in vacuum, and therefore its purification presented no special difficulties.

The purest samples of secondary oxide, which we obtained by double distillation under reduced pressure with a column containing glass rings and having an efficiency of 15 theoretical plates, used in our study had the following constants: b.p. 84 to 84.5° at 4 mm; n_D^{20} 1.4630-1.4635; d_4^{20} 0.951; M 168, (cryoscopic in benzene solution). Elementary composition (repeated determinations) $C_{10}H_{16}O_2$.

2. Determination of degree of unsaturation of the secondary oxide

The determination was effected by two methods: titration with benzoyl hydroperoxide according to Nametkin and Bryusov [6], and bromination by the method of MacIlliney with modifications by Virbyants and Meshcheryakova[7]. The results of both methods agreed. It was found that the molecule of the secondary oxide contains one ethylene bond.

3. Determination of the nature of the oxygen-carbon bonds in the secondary oxide

Determination of active hydrogen. Active hydrogen was determined by the method of Terentyev and Kireev [8] with the aid of Chugaev's reagent. It was found that the secondary oxide contains no active hydrogen.

Determination of peroxide oxygen. The freshly distilled secondary oxide did not liberate iodine from aqueous solutions of potassium iodide and did not give a color reaction with thiocyanate or with resin. Therefore it contains neither peroxide nor hydroperoxide oxygen.

Reaction of the α-oxide oxygen

Color reaction with pyridine. A drop of the secondary oxide was dissolved in ethanolic pyridine mixture (1:5). After 15 hours the original colorless, clear solution assumed a bright brown, and after 7 days a dark brown color, characteristic of α-oxide. Zimakov [9] points out that this is a very sensitive and specific test for α-oxides.

Interaction of the secondary oxide with manganese chloride. It is known that the similarity of α-oxides to the hydrohalogen acids is so great that they may decompose some salts of these acids with the formation of metal hydroxides [10]. It was found that our secondary oxide reacted very well with manganese chloride even in the cold. 3.3 g of secondary oxide was mixed in solution with 12 g of manganese chloride (crystalline hydrate) and 12 ml of ethanol in a test tube with a ground glass stopper. At the same time a blank experiment was carried out. After a day the tube with the oxide showed a copious precipitate of manganese hydroxide, and on the surface a layer of oil formed. The blank tube was unchanged. The hydroxide was filtered off, washed with ethanol, and dried to constant weight. 1.61 g of hydroxide was obtained. The filtrate was diluted with water and extracted with ether. The ethereal extract was washed with water and dried over calcium chloride. After the ether had been removed on the water-bath under reduced pressure, 1.53 g of a yellow oil with an agreeable fruity odor (n_D^{20} 1.4802) was obtained. The quantitative determination of chlorine in this oil carried out according to Stepanov gave the following results:

Found %: Cl 24.0
$C_{10}H_{17}O_2Cl$. Calculated %: Cl 17.4
$C_{10}H_{16}O_2Cl_2$. Calculated %: Cl 29.45

Consequently, the product of the interaction of secondary oxide with manganese chloride is dichlorohydrin mixed with unreacted secondary oxide.

Quantitative determination of α-oxide oxygen

The quantitative determination of α-oxide oxygen was effected by the method of Nikolya and Polter, described by Nazarov and Akhrem [11]. The method consists of rupturing the α-oxide rings with 0.2 N solution of dry hydrogen chloride in absolute ether. Nazarov and Akhrem successfully applied this method to the determination of α-oxide oxygen in keto dioxides, and they noted that the reaction of fission of the oxide rings proceeds slowly, requiring about 14 days. Our oxide was found to behave similarly. After 12 days we found in the secondary oxide only 1.03 oxide rings. Considerable increase in the length of the experiment led to no material change in the results.

Interaction of the secondary oxide with methanol

Since it was observed that the secondary oxide had α-oxide properties, we decided to make a further study of these properties. It is known that α-oxides can react with alcohols to form the corresponding monoalkyl ethers. The action is catalyzed by various acid reagents [9]. 28.1 g of secondary oxide dissolved in 60 ml of absolute methanol was gradually added to 60 ml of methanol containing 0.3 g of sulfuric acid, care being taken that the temperature did not exceed 40-45°. The reaction mixture was neutralized with the calculated amount of sodium methoxide. After removal of the excess alcohol and drying in vacuum, 38.4 g of reaction product was obtained. (If we assume that the secondary oxide contains two α-oxide rings, then the theoretical yield of the ether should amount to 38.8 g. Therefore, the actual yield of crude product amounts to 97.5% of theory.)

Distillation of 31.2 g of this crude product under reduced pressure in a Claisen flask gave 22.5 g of a fraction with b.p. 141-142° at 10 mm; n_D^{20} 1.4670, d_4^{20} 1.017. This was almost pure dihydroxydimethyl ether: M (Rast) in camphor 225; calculated, 232.

Found %: C 62.64; H 10.37.
$C_{10}H_{16}(OH)_2(CH_3O)_2$. Calculated %: C 62.07; H 10.33

By bromination one ethylene bond was found. A Zeisel determination showed 23.7, 23.9% of CH_3O. Two OH groups were found in the molecule by Terentyev's method, $C_{10}H_{16}(OH)_2(CH_3O)_2$. If the molecule of the addition product of methanol to the secondary oxide has two methoxide and two hydroxyl groups, it must be assumed that the initial secondary oxide is a dioxide.

Hydrogenation of the secondary oxide

Hydrogenation was carried out at room temperature under atmospheric pressure, an skeletonized nickel catalyst being used; this was prepared by the usual method of treating a nickel aluminum alloy with alkali.

In the experiment 20.1 g of secondary oxide, 50 ml of ethanol (as solvent) and a catalyst prepared from 35 g of nickel-aluminum alloy were used. (Capacity 200 ml; number of vibrations 184 per minute). The hydrogenation proceeded very smoothly at the rate of 120 ml per minute. A total of 8,100 ml of H_2 was absorbed. In theory, if we consider that the secondary oxide molecule has one ethylene bond and two α-oxide rings, 8,753 ml should be absorbed. Therefore, 2.78 moles of H_2 were added per mole of oxide. The catalyst was filtered off, the ethanol removed by distillation, and the hydrogenation product distilled under reduced pressure from a Claisen flask. 16.6 g of product was distilled. 13 g of a fraction which completely came over between 130 and 131° at 10 mm; n_D^{20} 1.4560; d_4^{20} 0.933, was obtained.

Found %: C 69.0, 69.0; H 12.2; 12.12

$C_{10}H_{20}(OH)_2$ Calculated %: C 69.0; H 12.65

This had no ethylene bonds. By Terentyev's method, two OH groups were found. Consequently, the main product of the addition of three moles of hydrogen to one mole of a secondary oxide is a saturated aliphatic terpene glycol of composition $C_{10}H_{20}(OH)_2$. This confirms that the secondary oxide itself is a terpene dioxide of the aliphatic series.

Hydration of the secondary oxide

37.7 g of secondary oxide was gradually added to 150 ml of decinormal aqueous sulfuric acid with vigorous stirring, care being taken to see that the temperature of the reaction mass did not exceed 35° (water cooling). The reaction mixture — a cloudy, bright-yellow liquid — was extracted four times with toluene. The last extract was entirely clear and colorless. The aqueous layer after the extraction consisting of a clear, colorless liquid, was neutralized with 6 g of barium carbonate. After a day the precipitated sulfur and excess barium carbonate were filtered off. The filtrate was concentrated under reduced pressure (25 mm) at 50°, and the residue was dried in vacuum to constant weight.

43.15 g of hydration product was obtained. If the secondary oxide molecule contains two α-oxide rings, then the theoretical amount of hydration product should be 45.7 g. Therefore, the yield amounts to 94.5% of theory.

The hydration product was a thick, resinous mass of a bright-yellow color, odorless, and with a bitter-sweet taste. On long storage (1.5 months) it gradually crystallized, forming a mass resembling crystallized honey. It was easily soluble in water and in alcohols. It was insoluble in diethyl ether, chloroform, and in benzene. After two recrystallizations from acetone and drying at 105°, a crystalline product with m.p. 124-125° was obtained in good yield; this resembled granulated sugar. Analysis of this crystalline product gave the following results:

Found %: C 58.72, 58.6; H 9.53, 9.64

$(C_{10}H_{16}(OH)_4$ Calculated %: C 58.82; H 9.80

Molecular weight (Rast, in camphor) 198; calculated M for $C_{10}H_{16}(OH)_4$ 204; found (Terentyev) OH groups, %: 31.2, 30.4; calculated % OH groups 33.3.

The crystalline hydration product contained one ethylene bond. Heating with acetic anhydride in the presence of anhydrous sodium acetate resulted in acetylation of only two hydroxide groups. The second two hydroxide groups did not acetylate under these conditions, but remained free. The hydration experiments were repeated several times with the same results. Thus, the experiments showed that the main hydration product of the secondary oxide is an unsaturated aliphatic tetrahydric terpene alcohol — tetrite — of composition $C_{10}H_{16}(OH)_4$. From this it must also be assumed that the secondary oxide is an aliphatic terpene α-dioxide.

SUMMARY

1. The course of the allo-ocimene (2,6-dimethyloctatriene-2,4,6) autoxidation has been studied. It has been found that the process proceeds in stages. The composition and properties of the intermediate products for the individual stages of the process have been described.

2. The chemical properties of a secondary oxide — the main intermediate product of the second autoxidation stage — have been studied. It was found to be an aliphatic terpene dioxide.

3. For the first time new aliphatic terpene derivatives have been obtained from the secondary oxide: an unsaturated tetrite, a saturated glycol, and a dihydroxy dimethyl ether.

4. A mechanism is proposed for the allo-ocimene oxidation process.

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THE SYNTHESIS OF 2-ALKYLNAPHTHO- and 2-ALKYLBENZOPYRANYL SALTS FROM β-CHLOROVINYLKETONES

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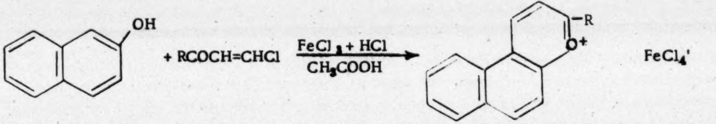
In one of our previous papers [1], it was shown that when methyl-β-chlorovinylketone and β-naphthol are allowed to interact in the presence of anhydrous ferric chloride and concentrated hydrochloric acid in acetic acid solution, a high yield of 2-methylnaphthopyranyl ferrichloride is obtained. Further studies showed that this reaction is quite general; under the same conditions, homologs of methyl-β-chlorovinylketone afford 2-alkylnaphthopyranyl ferrichlorides:

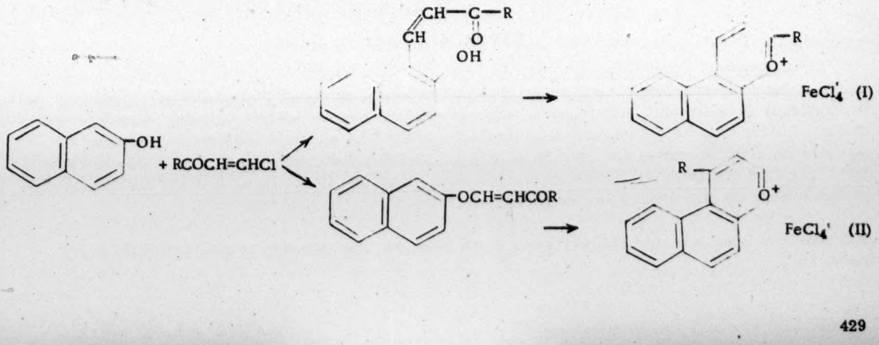


For the success of the reaction the purity of the ferric chloride is of great importance; we used anhydrous sublimed ferric chloride. With this the ferrichloride yields varied from 50 to 90%, depending on the nature of the radical in the alkyl-β-chlorovinylketone. When commercial hydrated ferric chloride was used, the reaction did not go in the required direction.

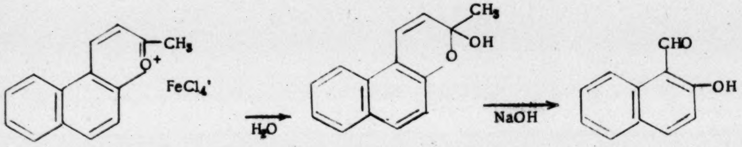
We attempted to prepare naphthopyranyl salts from β-naphthol and alkyl-β-chlorovinylketones, using other acid condensing agents. In the presence of perchloric acid no pyranyl salts were formed, but instead we obtained a colorless crystalline substance having m.p 230°, the structure of which we have not yet established. Condensation in the presence of sulfuric acid gave very small amounts of pyranyl salts, and this procedure did not seem likely to have any advantages.

The first homolog in the series of naphthopyranyl salts which we prepared, 2-methylnaphthopyranyl chloride, has recently [2] been prepared by the condensation of β-naphthol with methylethinylketone in the presence of ferric chloride. For this compound the authors give m.p. 141-143°; absolutely pure 2-methylnaphthopyranyl ferrichloride actually melts at 151-152°. The method we developed for the synthesis of alkylnaphthopyranyl salts has an advantage over the method of preparing them from alkylethinylketones: the starting materials, the alkyl-β-chlorovinylketones, are readily accessible, whereas the ethinylketones, especially the alkylethinylketones, are fairly difficult to obtain. The alkylnaphthopyranyl ferrichlorides obtained are red crystalline substances; they crystallize well from glacial acetic acid, and are soluble with difficulty in most organic solvents. When heated with hydroxylic solvents, they undergo changes apparently connected with the opening of the pyran ring. The color of the products varies from green to red, depending on the alkyl radical.

When β-naphthol reacts with alkyl-β-chlorovinyl ketone, the formation of two isomeric alkylnaphthopyranyl salts is theoretically possible, according to the following reactions (I) and (II)

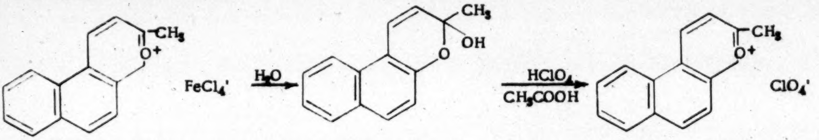


Up to now it has not been possible to exclude the second of these reactions, since we have previously shown [1] that alkyl-β-chlorovinylketones react with phenols to form β-aroxyvinylketones, and the cyclization of these under the reaction conditions could lead to the formation of the isomeric 4-alkylnaphthopyranyl ferrichlorides. In all cases we obtained only one compound from the reaction mixture. We proved the structure of the compounds obtained, using the first homolog as an example, by degradation. When the ferrichloride is treated with aqueous sodium acetate the pseudobase is formed, and when this is treated with alkali, it undergoes hydrolytic cleavage at the carbon-carbon double bond, as is usual for compounds of this type [3]; as a result 2-hydroxynaphthaldehyde-1 is formed, and we separated this from the reaction mixture:

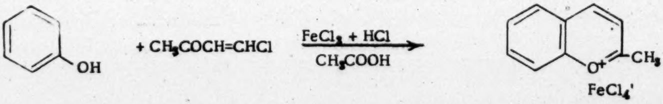


Therefore, for the compounds obtained, the 4-alkylnaphthopyranyl salt structure which should yield 1-acylnaphthol-2 on hydrolytic cleavage may be excluded. It should be mentioned that direct treatment of the pyranyl salt with alkali or ammonia, as is usually recommended for the benzopyranyl salts [3], in our case leads only to the formation of the crystalline substance with m.p. 230° which has already been mentioned.

The alkylnaphthopyranyl ferrichlorides obtained may be used as starting materials for the preparation of naphthopyranyl salts containing other anions. We prepared 2-methylnaphthopyranyl perchlorate from the corresponding ferrichloride; this was treated with an aqueous solution of sodium acetate and the ethereal solution of the resulting pseudo-base was then allowed to react with a mixture of acetic and perchloric acids, the perchlorate being separated in 52.9% yield:



The synthesis we have worked out for pyranyl salts may also be used for the preparation of benzopyranyl salts. Using phenol as an example, we showed that hydroxy derivatives of the benzene series also react with β-chlorovinylketones in the presence of ferric chloride and concentrated hydrochloric acid to form benzopyranyl salts:



Here the yield of pyranyl salt is much lower (15%); however, the reaction is mainly of interest because it shows the wide possibilities of synthesizing pyranyl salts from β-chlorovinylketones. The methylbenzopyranyl salt which separated had its methyl radical in position 2; we showed this by comparing the reaction product with the substance obtained by the known method [4] from methyl-o-hydroxycinnamylketone. The structure of alkylbenzopyranyl salts prepared from alkyl-β-chlorovinylketone is therefore similar to that of the alkylnaphthopyranyl salts obtained by the same method.

EXPERIMENTAL

1. Preparation of 2-methylnaphthopyranyl ferrichloride. To a solution of 0.5 g of β-naphthol in 5.0 ml of glacial acetic acid were added 0.5 g of methyl-β-chlorovinylketone and 5.0 ml of a solution of anhydrous ferric chloride in concentrated hydrochloric acid (the solution was prepared with the following proportions: 10.0 g of ferric chloride to 15.0 ml of concentrated hydrochloric acid). After an hour, the precipitate which had separated was collected and washed with a small quantity of glacial acetic acid, and then with absolute ether. Yield 1.0 g (74% of theoretical). After repeated recrystallization from glacial acetic acid, the 2-methylnaphthopyranyl ferrichloride was obtained as dark-green, acicular crystals with m.p. 151-152° *

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* In a previous paper a m.p. of 146° was given. It was found that after repeated recrystallization the m.p. rose to 152°.

Found %: C 42.85, 42.67; H 3.02, 2.98.

$C_{14}H_{11}OCl_4Fe$. Calculated %: C 42.75; H 2.82.

The compound dissolved readily in hot acetic acid, but was insoluble in benzene and in ether; it was decomposed by water.

II. Degradation of 2-methylnaphthopyranyl ferrichloride. Two grams of finely ground 2-methylnaphthopyranyl ferrichloride was mixed with 50.0 ml of water and 20.0 ml of saturated sodium acetate solution. The pseudobase which separated was extracted with ether. The ether was distilled off and 20% sodium hydroxide solution was added to the residue. The orange solution was boiled under reflux until nearly all the color had disappeared. 20% sulfuric acid was then added to the filtered solution. The precipitated 2-hydroxynaphthaldehyde-1 was collected on a filter and dried over calcium chloride in a vacuum desiccator; the m.p. was 80°. The literature [5] gives m.p. 81°.

The oxime of the aldehyde had m.p. 156°; the literature [6] gives 157°.

III. 2-Methylnaphthopyranyl perchlorate. 1.7 g of finely ground 2-methylnaphthopyranyl ferrichloride, prepared by Method I, was mixed with 70.0 ml water. To the mixture 20.0 ml of saturated sodium acetate solution was added. The reaction mixture was vigorously shaken. The pseudobase which separated was extracted with ether. To the ethereal extract 10.0 ml of glacial acetic acid was added, and the ether was removed by distillation. To the residue 10.0 ml of 70% perchloric acid was added. The contents of the flask were heated until all the residue had dissolved, after which the flask was allowed to stand overnight. 2-Methylnaphthopyranyl perchlorate separated in the form of dark-green crystals. Yield 0.7 g (52.9% of theoretical). After recrystallization from glacial acetic acid, the m.p. was 179-180°.

Found %: C 56.71, 56.85; H 3.53, 3.54.

$C_{14}H_{11}O_5Cl$. Calculated %: C 57.06; H 3.76.

The compound was readily soluble in glacial acetic acid, but insoluble in benzene and in ether; it was decomposed by water.

IV. 2-n-Propylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 1.6 g of n-propyl-β-chlorovinylketone, 2.0 g of β-naphthol, and 12.0 ml ferric chloride in concentrated hydrochloric acid, the whole being mixed in 20.0 ml of glacial acetic acid. Yield 5.5 g (93% of theoretical). After recrystallization from glacial acetic acid, 2-n-propylnaphthopyranyl ferrichloride was obtained as bright-green crystals with m.p. 124°.

Found %: C 45.48, 45.56; H 3.66, 3.59; Fe 13.23, 13.43.

$C_{16}H_{15}OCl_4Fe$. Calculated %: C 45.62; H 3.58; Fe 13.27.

V. 2-Isopropylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 10 g of isopropyl-β-chlorovinylketone, 1.2 g of β-naphthol, and 6.5 ml of solution of ferric chloride in concentrated hydrochloric acid, the whole in 15.0 ml of glacial acetic acid. Yield 2.5 g (71.4% of theoretical). After recrystallization from glacial acetic acid, 2-isopropylnaphthopyranyl ferrichloride was obtained as yellow acicular crystals. The compound melted at 100.5°, then solidified as the temperature was further raised and melted again at 157°.

Found %: C 45.78, 45.66; H 3.76, 3.66; Fe 13.22, 13.23.

$C_{16}H_{15}OCl_4$. Calculated %: C 45.62; H 3.58; Fe 13.27.

VI. 2-Isobutylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 1.1 g of isobutyl-β-chlorovinylketone, 1.0 g of β-naphthol, and 6.0 ml of solution of ferric chloride in concentrated hydrochloric acid, the whole in 10 ml of glacial acetic acid. Yield 2.2 g (73% of theoretical). After repeated recrystallization, 2-isobutylnaphthopyranyl ferrichloride was obtained as brilliant yellow platelets with m.p. 103°.

Found %: C 47.05, 46.96; H 3.68, 3.77; Cl 32.48, 32.65; Fe 12.62, 12.57.

$C_{17}H_{17}OCl_4Fe$. Calculated %: C 46.89; H 3.91; Cl 32.64; Fe 12.87.

VII. 2-n-Amylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 4.0 g of amyl-β-chlorovinylketone, 3.5 g of β-naphthol, and 20.0 ml of hydrochloric acid solution of ferric chloride, the whole in 30.0 ml of glacial acetic acid. Yield 5.0 g (50% of theoretical). After repeated recrystallization, 2-n-amylnaphthopyranyl ferrichloride was obtained as reddish-brown plates with m.p. 74°.

Found %: C 48.14, 48.18; H 4.42, 4.37; Cl 31.62, 31.65; Fe 12.22, 12.31.

$C_{18}H_{19}OCl_4Fe$. Calculated %: C 48.16; H 4.27; Cl 31.58; Fe 12.44.

VIII. 1-Methylbenzopyranyl ferrichloride. This was prepared as in Experiment I from 8.0 g of methyl-β-chlorovinylketone, 8.0 g of phenol, and 30.0 ml of hydrochloric acid solution of ferric chloride, the whole in

48.0 ml of glacial acetic acid. The precipitate was obtained after 5 hours. Yield 4.0 g (15% of theoretical). After recrystallization from glacial acetic acid, 2-methylbenzopyranyl ferrichloride was obtained as bilberry-red crystals with m.p. 125°. The literature [4] gives 118°.

IX. Synthesis of 2-methylbenzopyranyl ferrichloride by Decker's method. To a solution of 1.0 g of methyl-o-hydroxycinnamylketone [7] in 10.0 ml of glacial acetic acid, 10 ml of solution of anhydrous ferric chloride in concentrated hydrochloric acid was added. The reaction mixture was heated to boiling and allowed to stand overnight. The crystals which separated were filtered off and several times recrystallized from glacial acetic acid. Bilberry-red crystals were obtained with m.p. 124°; the literature [4] gives m.p. 118°.

SUMMARY

1. A new method of preparing 2-alkylnaphthopyranyl salts from the easily accessible alkyl-β-chlorovinylketones is described. The method makes it possible to prepare 2-alkylnaphthopyranyl salts in good yield.

2. It is shown that it is possible to convert the ferrichlorides obtained into the corresponding alkylnaphthylpyranyl perchlorates.

3. When the 2-methylnaphthopyranyls were treated with alkali, 2-hydroxynaphthaldehyde-1 was obtained; this proves the structure of the naphthopyranyl salts.

4. It is shown that phenol also reacts with methyl-β-chlorovinylketone to form 2-methylbenzopyranyl salts.

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THE ACTION OF PHOSPHORUS TRICHLORIDE ON THE ETHYL ESTERS OF ORTHOPROPIONIC AND ORTHOSILICIC ACIDS

B. A. Arbuzov and N. P. Bogonostseva

In Post's monograph "The Chemistry of the Aliphatic Orthoesters" [1], the results obtained by Bassett [2] on the action of phosphorus trichloride on orthoformic acid are given; this results — according to Bassett — in the formation of monoethyl phosphite; according to Arnold [3], whose results are also given, triethyl phosphitie is formed in this reaction:

$$3HC(OC_2H_5)_3 + PCl_3 \longrightarrow 3HCOOC_2H_5 + 3C_2H_5Cl + (C_2H_5O)_3P.$$

Examination of Arnold's paper shows that when phosphorus trichloride and orthoformic ester are reacted in equimolecular proportions ethyl chloride is evolved. From the reaction products Arnold separated a fraction boiling at 55-75° which, according to him, consisted of ethyl formate and phosphorus trichloride, and a fraction boiling at 150-190°, which he considered to be triethyl phosphite. Arnold gave no data to confirm the formation of triethyl phosphite. The same monograph describes Friedel and Ladenburg's [4] preparation of ethyl phosphite and ethyltrichlorosilane by the interaction of phosphorus trichloride and ethyl silicopropionate.

On consulting the actual paper of Friedel and Ladenberg, it was found that they only expected to obtain triethyl phosphite and ethyltrichlorosilane, but on carrying out the reaction with ethyl silicopropionate, they obtained a fraction boiling at 110-150°; but they did not succeed in separating a constant-boiling fraction from this.

In order to find if it were possible to obtain esters of phosphorous acid by reacting phosphorous trichloride and orthoesters, we reacted phosphorous trichloride with the ethyl esters of orthopropionic and orthosilicic acids. On reacting orthopropionic estet with phosphorus trichloride in equimolecular proportions (Arnold's conditions) we obtained a fraction corresponding to the chloranhydride of Menshutkin. This reaction was in accordance with the equation:

$$CH_3CH_2{-}C(OC_2H_5)_3 + PCl_3 = CH_3CH_2{-}COOC_2H_5 + C_2H_5Cl + C_2H_5OPCl_2$$

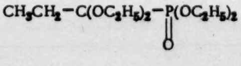
When the reagents were in the proportion of 2 moles of orthopropionic ester to 1 mole of phosphorus trichloride, a fraction was separated the constants and analysis of which corresponded to the chloranhydride of diethylphosphorous acid:

$$2CH_3CH_2{-}C(OC_2H_5)_3 + PCl_3 = 2CH_3CH_2{-}COOC_2H_5 + 2C_2H_5Cl + (C_2H_5O)_2PCl.$$

With a ratio of 3 moles of orthoester to 1 mole of phosphorus trichloride, as we have shown, triethyl phosphite is formed:

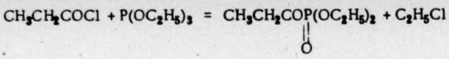
$$3CH_3CH_2{-}C(OC_2H_5)_3 + PCl_3 = 3CH_3CH_2{-}COOC_2H_5 + 3C_2H_5Cl + P(OC_2H_5)_3,$$

and this was proved by the constants of the phosphorous ester and by the formation with CuI of a complex crystalline compound, $CuI \cdot P(OC_2H_5)_3$ with m.p. 109-110° [5]. In the latter case, in addition to triethyl phosphite, a substance with the following constants was separated: b.p. 140-142° at 14 mm; d^{20}_{20} 1.0353; n^{20}_D 1.4324. The analysis and properties of this compound corresponded to the ethyl ester of the acetal of propionylphosphinic acid:



$$CH_3CH_2{-}C(OC_2H_5)_2{-}\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$$

In order to prove the structure of this compound, propionylphosphinic acid ester was prepared by the action of propionyl chloride on triethyl phosphite:

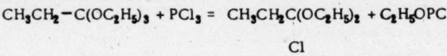


$$CH_3CH_2CO\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 \quad CH_3CH_2COCl + P(OC_2H_5)_3 = CH_3CH_2CO\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 + C_2H_5Cl$$

with the following constants: b.p. 100.5-102.5° at 8 mm; d_{20}^{20} 1.0893; n_D^{20} 1.4230. The semicarbazone had m.p. 160-162°.

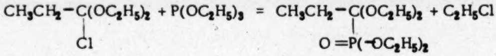
An attempt was made to obtain the acetal of propionylphosphinic ester by the action of orthoformic ester [6], but the results were negative. Then the substance with b.p. 140-142° at 14 mm, obtained by the interaction of orthopropionic ester and phosphorus trichloride, was carefully saponified in the cold. The saponification product gave a semicarbazone with m.p. 162-163°. These results show that the compound with b.p. 140-142° at 14 mm is the diethyl acetal of propionylphosphinic acid ester.

The formation of the acetal of propionylphosphinic acid ester may be considered as taking place in the following way: orthopropionic ester first reacts with phosphorus trichloride to form the chloro-ether according to the following equation:



$$CH_3CH_2-C(OC_2H_5)_3 + PCl_3 = CH_3CH_2\underset{Cl}{C}(OC_2H_5)_2 + C_2H_5OPCl_2$$

The chloro-ether reacts with the triethyl phosphite formed, giving the ester of propionylphosphinic acid acetal:



$$CH_3CH_2-\underset{Cl}{\underset{|}{C}}(OC_2H_5)_2 + P(OC_2H_5)_3 = CH_3CH_2-\underset{O=P(-OC_2H_5)_2}{\underset{|}{C}}(OC_2H_5)_2 + C_2H_5Cl$$

The possibility that the chloro-ether might be formed as an intermediate has already been mentioned by Arnold [3].

The reaction of phosphorus trichloride with ethyl orthosilicate did not yield such a clear picture. The best results were obtained with a ratio of 3 moles of orthosilicic ester to 4 of phosphorus trichloride. But even with this ratio, the only substance separated in the pure state was triethoxymonochlorosilane. Fractions were also obtained corresponding to Menshutkin's chloranhydride and to diethoxydichlorosilane, contaminated with products containing phosphorus. Triethylphosphite was not obtained.

EXPERIMENTAL

Reaction of 3 molecules of orthopropionic ethyl ester with 1 molecule of phosphorus trichloride

To 40 g of ethyl orthopropionic ester (b.p. 60° at 17 mm) 10.6 g of phosphorus trichloride was added. The mixture boiled up vigorously and the temperature rose to 70°. At first a white precipitate was formed, but as the trichloride was added, a colorless liquid formed. When all the trichloride had been added, the reaction mixture was heated for 2 hours on the water-bath. Distillation with a Widmer column afforded the following fractions:

Fraction I, with b.p. 22-25° at 16 mm (at atmospheric pressure it distilled at 98.5-99.5°); d_{20}^{20} 0.8938; $n_D^{20.1}$ 1.3860; yield 10.1 g. Corresponds to the ethyl ester of propionic acid.

Fraction II, b.p. 52 to 55° at 13 mm; d_{20}^{20} 0.9677; n_D^{20} 1.4101; yield 9.8 g. Corresponds to triethyl phosphite. Proved by the formation of the complex $CuI \cdot P(OC_2H_5)_3$, with m.p. 109-110° [5].

Fraction III, with b.p. 140-142° at 14 mm; d_{20}^{20} 1.0353; n_D^{20} 1.4324; yield 9.9 g. Corresponds to the diethyl acetyl of the ethyl ester of propionyl phosphinic acid.

Analysis of fraction III.

Found %: C 49.30; H 9.51; P 11.83 (Neiman); 11.87 (amperometric)

$C_{11}H_{25}O_5P$. Calculated %: C 49.25; H 9.3; P 11.6.

Saponification of Fraction III. To 1 g of the substance 1 ml of distilled water and 3 drops of concentrated HCl were added. The flask was closed with a cork and set aside. For the first three days the liquid layers did not mix. After standing for two weeks at room temperature the liquid became completely homogeneous. The water was distilled off under reduced pressure and the residue distilled at a temperature of 108-110° at 12 mm; n_D^{20} 1.4265; yield 0.4 g.

Preparation of the semicarbazone. To 0.2 g of the saponified product, 0.3 g of sodium acetate was added, together with a small quantity of absolute ethanol. To this solution an aqueous solution of 0.3 g of semicarbazide hydrochloride was added and then sufficient ethanol to dissolve the crystals completely. It was then stirred with a glass rod and allowed to stand. After standing for two months, clear white crystals separated as tablets — the inorganic part. On concentrating the aqueous layer, a yellow oil at first easily separated, and then white crystals in the form of granules appeared; these were insoluble in water and had m.p. 160-163°. The yield was insignificant.

Preparation of the ethyl ester of propionylphosphinic acid. To 28 g of triethyl phosphite, 15.5 g of propionyl chloride, b.p. 80-85°, was added dropwise. The reaction was carried out in an Arbuzov flask. Each drop of propionyl chloride produced a sizzling and an increase in temperature. The thermometer placed at the joint of the Arbuzov flask showed a temperature of 40°. When all the propionyl chloride had been added, hydrogen chloride was sucked off in vacuum and the mixture was distilled. There was then obtained:

Fraction I, with b.p. up to 100° at 8 mm; 1.6 g.
Fraction II, with b.p. 100.5° to 102.5° at 8 mm; 14.5 g; d_{20}^{20} 1.0893; n_D^{20} 1.4230.
Fraction III, residue, 3.4 g.

The residue could not be distilled and consisted of a colorless solid mass easily soluble in water.

On repeated distillation of parts of Fraction II, no constant boiling product could be obtained; the temperature gradually rose from 67° at 8 mm to 121° at 8 mm and only 30% was obtained in the fraction with b.p 100.5-102.5° at 8 mm having d_{20}^{20} 1.080; n_D^{20} 1.4201. Subsequent fractionations gave no fractions boiling within narrow temperature ranges.

Analysis of Fraction II for phosphorus

Found %: P 16.20, 16.27.
$C_7H_{15}O_4P$. Calculated %: P 15.98.

Reactions of the CO group with the ethyl ester of propionylphosphinic acid.

With nitroprusside of sodium. The product in small quantity was diluted with an equal volume of water, and a crystal of nitroprusside of sodium was added; to this solution was added 10% of sodium hydroxide solution. The solution became bright apple-green.

Preparation of the semicarbazone. In a test tube with the smallest possible quantity of water 0.65 g of semicarbazide hydrochloride was dissolved; in another tube 0.5 g of propionylphosphinic ester and 0.65 g of sodium acetate were placed, together with a small quantity of absolute ethanol. In the latter tube, the contents of the first tube were poured into the second, and absolute ethanol was added to dissolve the crystals completely. The mixture was then stirred with a glass rod and allowed to stand. After standing for a week, colorless crystals separated as tablets insoluble in water — the inorganic part. After concentration of the aqueous solution, white crystals in the form of granules insoluble in water, with m.p. 160-162°, were precipitated. Yield 0.4 g.

Attempt to prepare the diethyl acetal of the ethyl ester of propionyl phosphinic acid [6]. To 5 g of the ethyl ester of propionylphosphinic acid, 4.6 g of ethyl orthoformate and 5 g of absolute ethanol were added. The mixture was allowed to stand overnight at room temperature and then fractionated. The required fraction, boiling at a temperature of 140-142° at 14 mm, could not be separated. A fraction was separated with b.p. 118-119.5° 16 mm, in yield of 1 g; d_{20}^{20} 1.0715; n_D^{20} 1.4170.

Interaction of two molecules of ethyl orthopropionate with one molecule of phosphorus trichloride.

40 g of ethylorthopropionate was added to 15.7 g of phosphorus trichloride. Heat was evolved, and the solution came to a boil. When this process had ended, the mixture was heated for 2.5 hours on a water bath. A small white crystalline precipitate was obtained, and the solution assumed an almost green tinge. The reaction mixture was fractionated in a Widmer column.

There was obtained:

Fraction I, b.p. 99-100°; d_{20}^{20} 0.8889; n_D^{20} 1.3870; yield 21.5 g. Corresponds to ethyl propionate.

Fraction II, with b.p. 52-54° at 25 mm; d_{20}^{20} 1.0871; n_D^{20} 1.4344; yield 5.5 g. Corresponds to the chloranhydride of diethylphosphorous acid [7].

Analysis of phosphorus in Fraction II.

Found %: P 19.64, 19.75.
$C_4H_{10}O_2PCl$. Calculated %: P 19.87.

Interaction of one molecule of ethyl orthopropionate and one molecule of phosphorus trichloride

To 39.19 g of phosphorus trichloride, 50 g of ethyl orthopropionate was added. Evolution of heat accompanied by boiling was observed. When all the liquid had been added, a white precipitate formed. After boiling for two hours, the precipitate settled on the walls of the flask and assumed a yellow color. The reaction mixture was fractionated in a Widmer column. After three distillations, the following fractions were obtained.

Fraction I, b.p. 65-75°; 5.6 g.

Fraction II, b.p. 99-100.5°; 34 g; d_{20}^{20} 0.9772 ; n_D^{20} 1.3965. Corresponds to contaminated ethyl propionate.

Fraction III, b.p. 116-118°; 12 g; d_{20}^{20} 1.2373; n_D^{20} 1.4750. Corresponds to Menshutkin's chloranhydride [8].

Analysis of phosphorus in Fraction III.

Found %: P 21.09, 21.01

$C_2H_5OPCl_2$. Calculated %: P 21.08.

Interaction of three molecules of tetraethyl orthosilicate with four molecules of phosphorus trichloride

To 44.1 g of phosphorus trichloride, 50 g of tetraethyl orthosilicate was added. A trap was attached to collect the ethyl chloride. No visible signs of reaction were observed without heating. The reaction mixture was heated on the water bath for four hours at the temperature of boiling water. No ethyl chloride separated. The reaction mixture was fractionated in a Widmer column under reduced pressure and also at atmospheric pressure, and after three distillations the following fractions were obtained:

Fraction I, b.p. 116-118°; 27.5 g; d_4^{20} 1.3160. Corresponds to Menshutkin's chloranhydride [8].

Fraction II, b.p. 137-138°; 14.0 g; d_4^{20} 1.1290. Corresponds to diethoxy dichlorosilane [9], admixed with phosphorus-containing compounds.

Fraction III, b.p. 154-156;5°; 13.1 g; d_4^{20} 1.0460. Corresponds to triethoxy monochlorosilane [9].

Fraction IV, b.p. 63-86° at 26 mm; 7.2 g; d_4^{20} 1.0410.

Fraction V, a mixture with b.p. 120-150°; 8.8 g.

Analysis of phosphorus in Fraction 1 *

Found %: P 21.10

$C_2H_5OPCl_2$. Calculated %: P 21.08

Analysis of Fraction II.

Found %: P 6.6; SiO_2 31.92.

$C_4H_{10}O_2SiCl_2$. Calculated %: P none; SiO_2 31.74.

Analysis of Fraction III.

Found %: P none; SiO_2 31.10, 31.11.

$C_6H_{15}O_3SiCl$. Calculated %: P none; SiO_2 30.3.

Analysis of Fraction IV.

Found %: P 8.5; SiO_2 23.03.

$C_4H_{10}O_2PCl$. Calculated %: P 19.87; SiO_2 none.

SUMMARY

1. When three molecules of the ethyl ester of orthopropionic acid were reacted with one of phosphorus trichloride, the ethyl ester of propionic acid, triethyl phosphite, and the diethyl acetal of the ethyl ester of proponyl phosphinic acid were separated.

2. When two molecules of the ethyl ester of orthopropionic acid reacted with one molecule of phosphorus

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* All analyses for phosphorus in the presence of silica were carried out by the method of amperometric titration [10].

trichloride, the ethyl ester of propionic acid and the chloranhydride of diethylphosphorous acid were obtained.

3. When one molecule of the ethyl ester of orthopropionic acid reacted with one molecule of phosphorus trichloride, the ethyl ester of propionic acid and Menshutkin's chloranhydride were obtained.

4. When three molecules of the tetraethyl ester of orthosilicic acid reacted with four molecules of phosphorus trichloride, Menshutkin's chloroanhydride and triethoxy monochlorosilane were obtained.

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BASIC NOMENCLATURE AND CLASSIFICATION OF LOW-MOLECULAR WEIGHT ORGANO-SILICON COMPOUNDS

A. V. Topchiev and K. A. Andrianov

Principles for the classification of organo-silicon compounds have been repeatedly put forward in the literature. In 1905 [1], a terminology was proposed based on silane (SiH_4) termed "silicone", and (H_3SiOH), termed "silicanol". The names of all other compounds were derived from these. It was also proposed [2] that compounds containing the $Si-Si$ bond should be called "silicases", and those containing $Si-O-Si$, "silicates". Later, Stock [3] proposed a nomenclature based on silicon hydrides; and compounds containing silicon and carbon atoms were named like the corresponding carbon compounds but with the prefix "silico"; thus, $CH_3CH_2SiH_3$ was silicopropane, and so on. Recently, the proposals of an American commission on organo-silicon nomenclature have been published [4]; the proposed nomenclature differs from Stock's mainly in the substitution of the prefix "sil" for "silico". The naming of organic groups is based on the Geneva System. New group terms have been introduced, e.g., "trisilonyl" for $H_3Si-SiH_2-SiH_2-$. In 1950, Kreshkov [5] proposed a nomenclature containing a number of important refinements. Thus, instead of the American commission's term "silazine" for nitrogen-containing compounds of the type $R_3SiNH[SiR_2NH]SiR_3$, he recommends "silamine".

In the nomenclatures discussed above, much attention is devoted to inorganic silicon compounds; this is especially so in the proposals of Stock and those of the American commission. For this reason, a large number of terms for inorganic atom groups are introduced, for example, $H_2Si<$ sililidine, $H_3SiNHSiH_2NH$ disilazanilamino, $H_3SiNHSiH_2O$ disilazanoxy, H_3SiSiH_2NH disilanilamino, etc. Many of these groups do not occur in organosilicon molecules, and they needlessly complicate nomenclature and terminology and make it difficult for the reader to study the organosilicon compounds.

At present the number of organosilicon compounds is considerable and it is growing every year. A separate classification and nomenclature are needed for organosilicon compounds, unencumbered by the nomenclature of compounds which should be considered in the inorganic chemistry of the silicons. We put forward the following basic classification and nomenclature for the organosilicon compounds, i.e., for silicon compounds which have carbon in addition to other elements as an essential constituent of the molecule.

The classification of low molecular weight organosilicon compounds which we put forward below is based on a rational nomenclature. The names of the simplest (first) compounds in a given class are used as the basis of the names of the compounds in that class. The silicon hydrides are used with advantage as starting materials in the classification, and all the remaining compounds are treated as derivatives of these, i.e., as substances derived from them by replacing one, two, three, or four hydrogen atoms by organic radicals or organic atom groups, and for certain classes of compounds with the simultaneous replacement of hydrogen by various atom or functional groups. The silicon hydrides constitute a class of compounds in which the silicon atoms are joined either to hydrogen or to other silicon atoms.

The general formula of the saturated silicon hydrides is Si_nH_{2n+2}. The simplest representative of this class of compound of silicon with hydrogen, SiH_4, is termed silane, its homolog $H_3Si-SiH_3-$ disilane, $H_3Si-H_2Si-SiH_3-$ trisilane, $H_3Si-SiH_2-SiH_2-SiH_3$ tetrasilane, and so on. Thus, the silicon hydrides form a homologous series, in which each successive member differs from the preceding one by the group SiH_2 (homologous difference).

When one or several hydrogen atoms in the homologous silicon hydride series is replaced by radicals or organic atoms groups such as

Radicals

Methyl CH_3-
Ethyl C_2H_5-
Propyl C_3H_7-
Butyl C_4H_9-
Phenyl C_6H_5-
Tolyl $CH_3C_6H_4-$
Benzyl $C_6H_5-CH_2-CH_2-$
Vinyl $CH_2{=}CH-$
Naphthyl $C_{10}H_7-$
Ethinyl $CH{\equiv}C-$
Chlorophenyl C_6H_4Cl-
Chloroethyl $ClCH_2CH_2-$
Chloromethyl $ClCH_2-$
etc.,

Atomic groups

Acetyl CH_3CO-
Propionyl CH_3CH_2CO-
Benzoyl C_6H_5CO- etc.
Methoxy CH_3O-
Ethoxy C_2H_5O-
Phenoxy C_6H_5O- etc.

Acetamido $-CH_2CO-NH-$
Toluyl $CH_3C_6H_4-CO-$
Anilino C_6H_4NH-
etc.

and hydrogen atoms joined to silicon are simultaneously replaced by functional groups: X (any halogen) $-OH$, $-NH_2$, O, etc. (oxygen is termed "oxy" to distinguish it from the OH-group, which is called "hydroxy") a corresponding homologous series is formed, consisting of halogen-containing organosilicon compounds, amines, etc. The position of the substituent groups in the aromatic nucleus is described in the usual way.

The following division of organosilicon compounds into large classes or series is most suitable for their study at the present time.

1. Substituted silanes

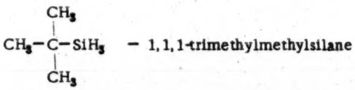
This class of compounds is formed by replacing one or several hydrogen atoms in the simple silicon hydrides SiH_4 or $H_3Si \cdot SiH_3$, etc., by the same or different radicals of the general fromula

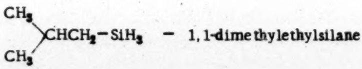
$$C_nH_{2n+1},\quad C_nH_{2n},\quad C_nH_{2n-1},\quad C_nH_{2n-7},\ \text{etc.}$$

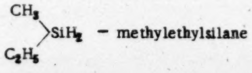
If one radical is attached to the silicon atom, the compound is termed a monosubstituted silane, with two – a disubstituted, with three – a trisubstituted, and with four – a tetrasubstituted silane.

Substituted silanes having different radicals on the silicon atom are called mixed substituted silanes. The radical is named according to the accepted rules of organic nomenclature. Therefore, the names of the substituted silanes are derived from the name of the radical or radicals with the ending silane; hydrogen is not pronounced, for example:

$CH_3-CH_2-CH_2-CH_2-SiH_3$ – butylsilane


$(CH_3)_3C-SiH_3$ – 1,1,1-trimethylmethylsilane


$(CH_3)_2CHCH_2-SiH_3$ – 1,1-dimethylethylsilane


$(CH_3)(C_2H_5)SiH_2$ – methylethylsilane

$ClCH_2-SiH_3$ – 1-chloromethylsilane
$ClCH_2CH_2-SiH_3$ – 2-chloroethylsilane
$(CH_3)_3Si \cdot Si(CH_3)_3$ – hexamethyldisilane
$(CH_3)_3Si \cdot Si(CH_2CH_3)_3$ – 1-trimethyl-2-triethyldisilane

2. Esters of orthosilicic acid

Orthosilicic acid esters are formed when hydrogen in SiH_4 is replaced by organic atom groups, i.e., by alkoxy or aryloxy groups of the general formula $C_nH_{2n+1}O-$, $C_nH_{2n}O-$, etc. The name of the ester is composed from the name of the organic atom group, the ending silane and the prefixes di-, tri-, tetra- indicating the number of organic atom groups joined to silicon, for example $(CH_3O)_4Si$ –tetramethoxysilane; $(CH_3O)_2-Si-(OC_2H_5)_2$ –dimethoxydiethoxysilane; $C_6H_5O-Si-(OCH_3)_3$ –phenoxytrimethoxysilane, etc.

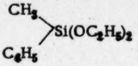
3. Halogen esters of orthosilicic acid

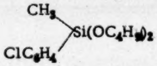
Halogen esters of orthosilicic acid are formed by replacing one, two, or three hydrogen atoms in silicon hydride SiH_4 by organic atom groups, i.e., by alkoxy groups of the general formula $C_nH_{2n+1}O-$ or aryloxy groups of the general formula $C_nH_{2n-7}-O-$ etc., while at the same time one, two, or three hydrogen atoms in SiH_4 are replaced by the same or different halogens (F, Cl, Br, and I). The halogen ester name is composed from the names of the organic groups, the halogen, and the ending silane. The number of atoms or groups joined to silicon is also indicated, for example $(C_2H_5O)_3-SiCl$ — triethoxychlorosilane, $(C_2H_5O)(CH_3O)SiCl_2$ — ethoxymethoxydichlorosilane, etc.

4. Substituted esters of orthosilicic acid

Substituted esters of orthosilicic acid are formed by replacing one or more hydrogen atoms in the simplest silicon hydride, SiH_4, by the same or different organic radicals C_nH_{2n-1}, C_nH_{2n-7}, etc., while other hydrogen atoms joined to silicon are at the same time replaced by the same or different alkoxy or aryloxy groups of the general formula $C_nH_{2n+1}-O-$, $C_nH_{2n-5}-O-$, etc. If one radical is joined to the silicon atom the compound is termed a monosubstituted ester of orthosilicic acid; with two radicals, the corresponding disubstituted, and with three radicals, a trisubstituted orthosilicic ester. The names of the substituted orthosilicic esters are composed from the name of the organic radical, the names of the alkoxy or aryloxy groups (organic atom groups), and the ending silane. The number of organic radicals and the number of organic atom groups joined to silicon are indicated, for example:

$CH_3Si(OC_2H_5)_3$ — methyltriethoxysilane


$\begin{matrix}CH_3\\ C_6H_5\end{matrix}\!>\!Si(OC_2H_5)_2$ — methylphenyldiethoxysilane

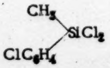

$\begin{matrix}CH_3\\ ClC_6H_4\end{matrix}\!>\!Si(OC_4H_9)_2$ — methyl-3-chlorophenyldi-n-butoxysilane

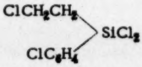
$ClCH_2CH_2-Si(OCH_2CH_2Cl)_3$ — 2-chloroethyltri-2-chloroethoxysilane, etc.

5. Alkyl and arylhalogenosilanes

Alkyl- and arylhalogenosilanes are formed by replacing one, two, or three hydrogen atoms in siliconhydride SiH_4 or $H_3Si\cdot SiH_3$ by organic radicals while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by halogen (chlorine, fluorine, bromine, or iodine). If one radical is joined to the silicon atom, the compounds are called monoalkyl-(aryl)halogenosilanes; with two radicals, dialkyl-(aryl)halogenosilanes; and with three radicals, trialkyl-(aryl)halogenosilanes. The names of the alkyl- and arylhalogenosilanes are composed from the name of the organic radical, the name of the halogen, and the ending silane. The number of radicals is also indicated as well as the number of halogen atoms and the names of the other atoms and groups.

$C_6H_5SiCl_3$ — phenyltrichlorosilane

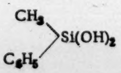

$\begin{matrix}CH_3\\ ClC_6H_4\end{matrix}\!>\!SiCl_2$ — methylchlorophenyldichlorosilane

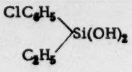

$\begin{matrix}ClCH_2CH_2\\ ClC_6H_4\end{matrix}\!>\!SiCl_2$ — 2-chloroethylchlorophenyldichlorosilane, etc.

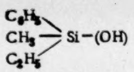
6. Organosilane hydroxyderivatives

Hydroxy derivatives of the organosilanes are formed by replacing one, two, or three hydrogen atoms in silicon hydride by organic radicals, while the remaining one, two, or three hydrogen atoms are replaced by hydroxyl groups. The terms mono-, di-, trihydroxylsilane derivative are used, according to the number of radicals joined to silicon. The name of the hydroxylsilane derivative is composed of the name of the organic radical, silane, and hydroxyl. The hydroxyl group is termed "hydroxy". The number of radicals and the number of hydroxyl groups, as well as the names of the atoms or atom groups in the radical are also indicated, for example:

$(C_2H_5)_2Si(OH)_2$ — diethyldihydroxysilane


$\begin{matrix}CH_3\\ C_6H_5\end{matrix}\!>\!Si(OH)_2$ — methylphenyldihydroxysilane

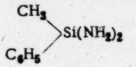

$\begin{matrix}ClC_6H_5\\ C_2H_5\end{matrix}\!>\!Si(OH)_2$ — chlorophenylethyldihydroxysilane



– phenylmethylethylhydroxysilane, etc.

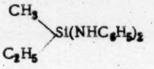
7. Alkyl- and arylaminosilanes

Alkyl- and arylaminosilanes are formed by replacing one, two, or three atoms of hydrogen in silicon hydride by organic radicals while the remaining one, two, or three hydrogen atoms in the same hydride are replaced by amino groups or by inorganic atom groups containing amino groups. Mono-, di-, and trialkyl (aryl)-aminosilanes are differentiated, according to the number of radicals joined to silicon in the molecule. The names of the alkyl(aryl)aminosilanes are composed from the names of the organic radical and the amino group, and the ending silane. For example:



– methylphenyldiaminosilane

$(CH_3)_3SiNHCH_3$ – trimethylmethylaminosilane



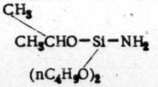
– methylethyldiphenylaminosilane

$(CH_3)_3SiNHSi(CH_3)_3$ – hexamethylaminodisilane

$(CH_3)_3SiCH_2NH_2$ – trimethylaminomethylsilane.

8. Alkoxy(aryloxy)aminosilanes

Alkoxy-(aryloxy)aminosilanes are formed by replacing one, two, or three hydrogens in silicon hydride SiH_4 by organic atom groups, i.e., by alkoxy-(aryloxy) groups of the general formula $C_nH_{2n+1}-O-$, $C_nH_{2n-7}O-$, etc., while the remaining hydrogen atoms are replaced by amino groups. The names of the alkoxy-(aryloxy)aminosilanes are composed from the name of the organic atom group and the amino group, and the ending silane, together with the prefixes di- and tri-, indicating the number of organic atom groups and amino groups joined to silicon, for example:

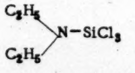


– isopropyloxydi-n-butyloxyaminosilane

$(C_4H_9O)_3SiNH_2$ – tri-tertiary butoxyaminosilane, etc.

9. Alkyl- and arylhalogenoaminosilanes

Alkyl- and arylhalogenoaminosilanes are formed by replacing one, two, or three hydrogen atoms in the simplest silicon hydride by organic atom groups containing nitrogen, while the remaining one, two, or three hydrogen atoms are replaced by halogen (chlorine, fluorine, bromine, or iodine). The names of alkyl-arylhalogenoaminosilanes are composed from the name of the organic atom group, the name of the halogen, and the ending silane, for example:

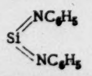


– diethylaminotrichlorosilane

$(C_6H_5NH)_2SiCl_2$ – diphenylaminodichlorosilane, etc.

10. Alkyl-aryliminosilanes

Alkyl-(aryl)iminosilanes are formed by replacing all the hydrogens in silicon hydride SiH_4 by imino groups $=NR$, or two hydrogens by an imino group and the remaining two by organic radicals or atom groups or by other atoms. The names of these compounds are composed of the radical name, the names of the organic groups, and the name of the imino group with the ending silane, for example:



– diphenyliminosilane

$(C_6H_5NH)_2Si=NC_6H_5$ — diphenylaminophenyliminosilane

$(C_6H_5)_2Si=N(C_6H_5)$ — diphenylphenyliminosilane

11. Silicon isocyanates

The silicon isocyanates are formed by replacing one, two, three, or four hydrogen atoms in silicon hydride SiH_4 by the group $-N=C=O$, while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by radicals, organic atom groups, or any other atom. The names of the silicon isocyanates are composed from the radical or organic atom group name, the name of the isocyanate group, and the ending silane. The number of radicals, organic atom groups, and the number of isocyanate groups are also indicated, for example:

$(CH_3)_2Si(NCO)_2$ — dimethyldiisocyanatesilane, etc.

The names of the silicon isothiocyanates are constructed in the same way, but the prefix "thio" is used, for example:

$(C_2H_5)Si(NCS)_3$ — ethyltrithioisocyanatesilane

12. Organometallic compounds of silicon

The organometallic compounds of silicon are formed by replacing one or more hydrogen atoms in SiH_4 by a metal (Na, K, Li, etc.), while the remaining three hydrogen atoms in the same silicon hydride are replaced by radicals, organic atom groups, or by any other atom. The names are composed from the radical name, the name of the atom group or the other atom, the name of the metal and the ending silane. The number of groups, radicals, etc. is also indicated, for example:

$(CH_3)_3SiLi$ — trimethyllithiumsilane

$(CH_3)_3SiOLi$ — trimethyllithiumoxysilane, etc.

13. Thioethers

Thioethers are formed by replacing one, two, three, or four hydrogen atoms in SiH_4 by the groups $C_nH_{2n+1}S-$, $C_nH_{2n-7}S-$, while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by radicals, by organic atom groups, or by other atoms or groups. The names of the thioethers are composed from the name of the thio group, the number of thio groups present, and the names of the radicals, organic atom groups, or other atoms. In addition, the number of these is indicated, for example:

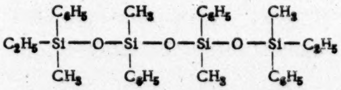
$(C_2H_5S)_3SiC_6H_5$ — trithioethylphenylsilane

$(BrC_6H_4S)_4Si$ — tetra-4-bromophenylthiosilane

$[(CH_3)_3(CS)_3Si]_2O$ — hexatertiary butylthiodisiloxane

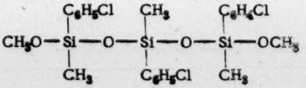
14. Organosiloxanes

When organosilicon hydroxy derivatives undergo condensation, compounds are formed whose molecules contain siloxane $Si-O-Si$ groups of atoms. These compounds, which are characterized by a cyclic or a chain molecular structure, are formed by the linking of alternate atoms of silicon and oxygen; we call them organosiloxanes. The classification and nomenclature of the high molecular weight compounds, the "organopolysiloxanes", and others will be given in a later paper. The names of the organosiloxanes are composed from the names of the radical or organic atom groups and their number, the number of siloxane groups in the molecule, and the ending — siloxane. The positions of the organic radicals and atom groups are also indicated, for example:



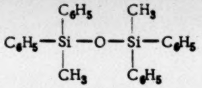
$$\begin{array}{ccccccccccccc} & & C_6H_5 & & & & CH_3 & & & & C_6H_5 & & & & CH_3 & & \\ & & | & & & & | & & & & | & & & & | & & \\ C_2H_5 & - & Si & - & O & - & Si & - & O & - & Si & - & O & - & Si & - & C_2H_5 \\ & & | & & & & | & & & & | & & & & | & & \\ & & CH_3 & & & & C_6H_5 & & & & CH_3 & & & & C_6H_5 & & \end{array}$$

1,4-diethyl-1,2,3,4-tetraphenyl-1,2,3,4-tetramethyltetrasiloxane



$$\begin{array}{ccccccccccc} & & C_6H_5Cl & & & & CH_3 & & & & C_6H_4Cl & & \\ & & | & & & & | & & & & | & & \\ CH_3O & - & Si & - & O & - & Si & - & O & - & Si & - & OCH_3 \\ & & | & & & & | & & & & | & & \\ & & CH_3 & & & & C_6H_5Cl & & & & CH_3 & & \end{array}$$

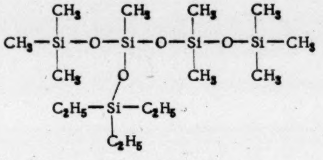
1,3-methoxy-1,2,3-chloro-3-phenyl-1,2,3-trimethyltrisiloxane



$$\begin{array}{ccccc} & C_6H_5 & & CH_3 & \\ & | & & | & \\ C_6H_5- & Si & -O- & Si & -C_6H_5 \\ & | & & | & \\ & CH_3 & & C_6H_5 & \end{array}$$

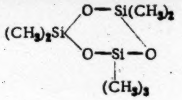
1,2-phenyl-1,2-methyl-1,2-phenyldisiloxane , etc.

When the organosilicon compound has a branched chain, the naming follows the principles usually employed for organic compounds, for example:

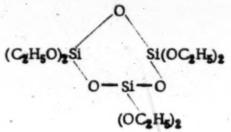


1,2,3,4-nonamethyl-2-triethylsiloxytetradisiloxane

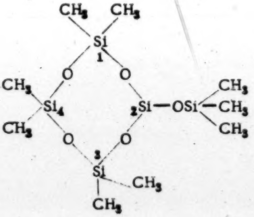
The prefix cyclo is used for cyclic organosiloxanes, for example:



— hexamethylcyclotrisiloxane

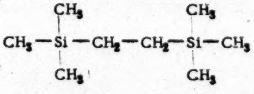


— hexamethylcyclotrisiloxane, etc.



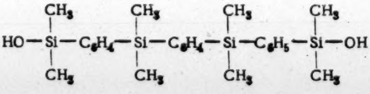
— 1,2,3,4-heptamethyl-2-trimethylsiloxycyclotetrasiloxane

Compounds with mixed chains, the molecules of which have silicon atoms joined to one another by divalent radicals or organic atom groups, have names derived from the radical or group names, for example:



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3- & Si & -CH_2-CH_2- & Si & -CH_3 \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

— ethylenehexamethyldisilane



$$\begin{array}{ccccccccc} & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & & | & \\ HO- & Si & -C_6H_4- & Si & -C_6H_4- & Si & -C_6H_5- & Si & -OH \\ & | & & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & & CH_3 & \end{array}$$

— triphenylene-1,4-hydroxy-1,1,2,2,3,3,4,4,-octamethyltetrasilane.

SUMMARY

1. A classification and nomenclature for the low-molecular-weight organosilicon compounds are proposed.
2. The names of the simplest (first) compounds in a given class are proposed as a basis for naming low-

molecular weight organosilicon compounds. The silicon hydrides are used as fundamental substances in the classification, and all other compounds are regarded as derivatives of these.

Received September 18, 1952

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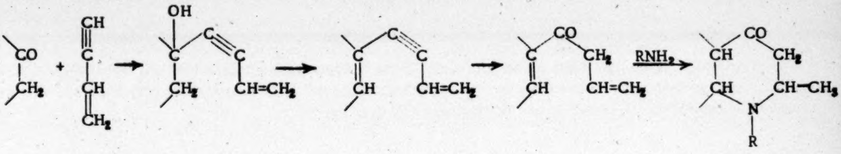
ACETYLENE DERIVATIVES

COMMUNICATION 150. HETEROCYCLIC COMPOUNDS

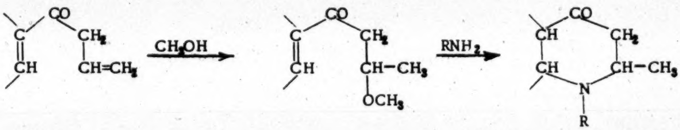
XXVI. THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS CONTAINING A CONDENSED 4-PIPERIDONE NUCLEUS

I. N. Nazarov, L. I. Ukhova, and V. A. Rudenko

The synthesis of 4-piperidones is of considerable interest, because they are important intermediates for the preparation of many pharmaceutical products of high analgesic, spasmolytic, and anesthetic activity. A few years ago a new simple method for the synthesis of 4-piperidones, starting from vinylallylketones [1] and ammonia or primary amines, was developed in our laboratory. The complete route to the 4-piperidones by this method may be illustrated as follows.

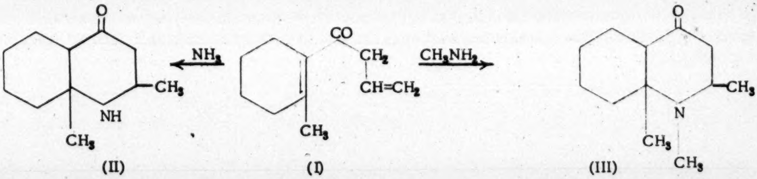


The 4-piperidones are also easily obtained by the action of ammonia or primary amines on the corresponding methoxyketones which are formed by the addition of methanol to vinylallylketone.



By means of this reaction, numerous 4-piperidones with various aliphatic and aromatic substituents in the piperidine nucleus were prepared. It was of interest to find if this method was applicable to the preparation of more complex polycyclic compounds containing the condensed 4-piperidone nucleus and angular methyl groups. We have therefore studied the reaction of ammonia and methylamine with various allyl-Δ^1-cyclenylketones and their corresponding methoxyketones.

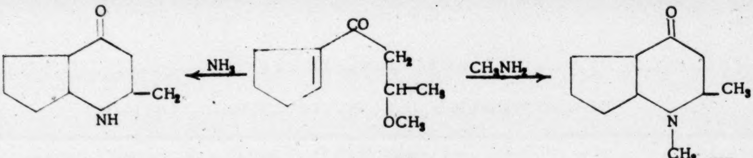
2,9-Dimethyl-4-ketodecahydroquinoline (II) and 1,2,9-trimethyl-4-ketodecahydroxyquinoline (III) were obtained in about 80% yield by the interaction of allyl-2-methyl-Δ^1-cyclohexenylketone (I) [2] with ammonia and methylamine.



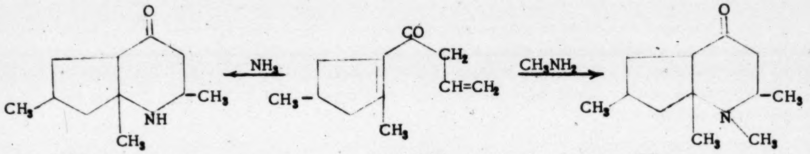
(II) (I) (III)

By the interaction of β-methoxypropyl-Δ^1-cyclopentenylketone (IV) [3] with ammonia and methylamine, 2-methyl-4-ketoperhydro-1-pyrindine (V) and 1,2-dimethyl-4-ketoperhydro-1-pyrindine (VI) are obtained in about 80% yield. (See top of following page.)

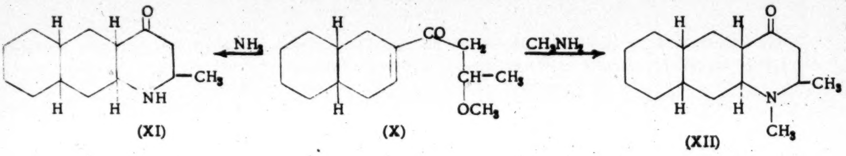
By the interaction of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) and its corresponding methoxyketone [4] with ammonia and with methylamine, 2,6,7a-trimethyl-4-ketoperhydro-1-pyrindine (VIII) and 1,2,6,7a-tetra-

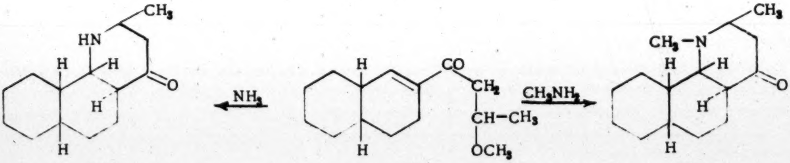

(V) (IV) (VI)

methyl-4-ketoperhydropyrindine (IX) are obtained:


(VIII) (VII) (IX)

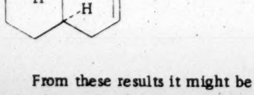
The action of ammonia and methylamine on β-methoxypropyl-2-octalylketone (X) and (Xa), which was obtained from cis-β-decalone, gave 2-methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa) and 1,2-dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or (XIIa):


(XI) (X) (XII)


(XIa) (Xa) (XIIa)

Hückel and Friedrich [5] have shown that dehydration of cis-β-decalones gives a mixture of Δ^1- and Δ^2-octalins, the relative quantities varying with the dehydrating agent.

Nazarov and Burmistrova [6] showed that vinylethynyl alcohol, obtained by the condensation of trans-β-decalone with vinylacetylene, also gives a mixture of the two 2-vinylethynyloctalines in almost equal proportions on dehydration: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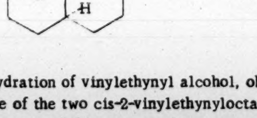


From these results it might be expected that in our dehydration of vinylethynyl alcohol, obtained by the condensation of cis-β-decalone with vinylacetylene, a mixture of the two cis-2-vinylethynyloctalins, Δ^1- and Δ^2-, would be obtained; on dehydration these would give a mixture of the corresponding two cis-allyl-2-octalylketones. We therefore attempted to separate these ketones, in order to cyclize the individual compounds with ammonia and methylamine. However, we did not succeed in separating either the cis- or the trans-allyl-2-octalylketone, since they did not crystallize even when cooled to −75°.

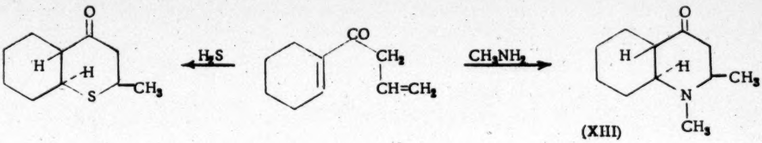
Since the cyclization product of the methoxyketones (X) or (Xa) with methylamine gave only one picrolonate with m.p. 201-203°, it may be supposed that in this cyclization one tricyclic ketone (XII) or (XIIa) is mainly formed, and the second is either not formed at all or is present in negligible quantity so that its separation is difficult.

The cyclization product of the methoxyketone (X) or (Xa) with ammonia did not give crystalline derivatives with either picric or picrolonic acid even on long standing. Since the position of the double bond in the methoxyketone (X) or (Xa) has not been proved, we ascribe formula (XII) or (XIIa) to the 1,2-dimethyl-4-ketoperhydrobenzoquinoline obtained, and formula (XI) or (XIa) to the 2-methyl-4-ketoperhydrobenzoquinoline.

The N-methylated compounds (III), (VI), (IX), and (XII) or (XIIa) were freed from impurities in the form of the corresponding imines [7] before analysis, by heating on the water bath with dilute hydrochloric acid, and after the usual treatment they were separated in the pure state.

In order to establish the steric structure of the 4-ketodecahydroquinolines (II), (III), and (XIII) obtained, these were heated with methanolic sodium methoxide. In all cases the starting material was recovered from the reaction mixture; this was proved by the fact that mixed samples of the picrates showed no depression in the melting points. By analogy with the α-decalones [8], the inability of the 4-ketodecahydroquinolines (II), (III), and (XIII) to isomerize under the influence of sodium methoxide may be taken as proof of the trans-configuration of these ketones.

Consequently, when allyl-Δ^1-cyclohexenylketones are cyclized with ammonia and primary amines, a piperidine nucleus joined at the trans position to another ring is formed; this was shown previously in our laboratory for the cyclization of the allyl-Δ^1-cyclohexenylketone with hydrogen sulfide [9]:



(XIII)

There is no doubt that the 4-ketoperhydrobenzoquinolines (XI) and (XII) also have the trans structure at the position where the 4-piperidone nucleus is fused with decalin.

It is also probable that the 4-ketoperhydro-1-pyrindines (V), (VI), and (IX) also have the trans structure; they did not change on heating with sodium methoxide, as was shown by the mixed melting point of the picrates.

Finally, it should be mentioned that the synthesis of 4-piperidones from the most diverse vinylallylketones, ammonia, and primary amines is the most general and the simplest method at present available for preparing these interesting and important compounds. It enables 4-piperidones with different nuclear substituents to be obtained, and also polycyclic compounds containing a condensed 4-piperidone nucleus and angular alkyl groups.

EXPERIMENTAL

1,2,9-Trimethyl-4-ketodecahydroquinoline (III)

A solution of 300 g of allyl-2-methyl-Δ^1-cyclohexenylketone (I) (m.p. 126-128° at 11 mm; n_D^{18} 1.4885 [2]) and 420 g of 33% aqueous methylamine in 270 ml of methanol was heated in a sealed metal tube at 60-70° for 7 hours. The tube was opened, the methanol and excess methylamine distilled off on the water bath under slightly reduced pressure, the residue acidified with hydrochloric acid (1:1), and the neutral products extracted with ether. The reaction product was separated by means of solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. There was obtained 254 g of 1,2,9-trimethyl-4-ketodecahydroquinoline (III) with b.p. 110-115° at 4 mm; n_D^{19} 1.5020. In order to remove possible imino-derivative impurities [7], 20 g of the compound was mixed with 30 ml of dilute hydrochloric acid (1:3) and heated for 1 hour on the boiling water bath. After cooling with ice water, the solution was saturated with solid alkali, and the base was extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had been distilled off. The product consisted of 15.1 g of pure 1,2,9-trimethyl-4-ketodecahydroquinoline in the form of a colorless, mobile liquid with a typical amine odor and b.p. 103-104° at 3 mm; n_D^{20} 1.5018; d_4^{20} 1.004; found MR 57.33; calculated MR 57.17.

Found %: N 7.19, 7.33.
$C_{12}H_{21}ON$. Calculated %: N 7.12

After recrystallization from aqueous ethanol, the picrate melted at 195-196°.

Attempt to isomerize 1,2,9-trimethyl-4-ketodecahydroquinoline

A solution of 0.15 g of metallic sodium in 65 ml of methanol was added to 5.4 g of 1,2,9-trimethyl-4-ketodecahydroquinoline (b.p. 103-104° at 3 mm; n_D^{20} 1.5018). The solution was refluxed for 5 hours, and then neutralized with acetic acid, after which the methanol was distilled off. The residue was dissolved in 8 ml of water, the solution was saturated with potash, the product extracted with ether, dried over sodium sulfate, and distilled under reduced pressure. Four grams of the starting 1,2,9-trimethyl-4-ketodecahydroquinoline with b.p. 106-107° at 3 mm; n_D^{20} 1.4995 was obtained. The picrate melted at 194-195° and gave no depression with the picrate of the starting material.

2,9-Dimethyl-4-ketodecahydroquinoline (II)

A solution of 30 g of allyl-2-methyl-Δ^1-cyclohexenylketone, (b.p. 126-128° at 11 mm; $n_D^{18.5}$ 1.4884 [2]), and 70 g of 30% aqueous ammonia in 120 ml of methanol was heated in a sealed metal tube for 6 hours at 70-75°. The methanol and excess ammonia were distilled off under reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral product extracted with ether. The base was carefully separated, with ice-water cooling, by means of solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been first distilled off. The product, 26 g of 2,9-dimethyl-4-ketodecahydroquinoline (II), was a colorless mobile liquid with a weak ammoniacal odor and b.p. 99-100° at 3 mm; n_D^{20} 1.5021; d_4^{20} 1.015; found MR 52.49; calculated MR 52.21.

Found %: N 7.42, 7.29.
$C_{11}H_{19}ON$. Calculated %: N 7.72.

The picrate on recrystallization from ethanol melted at 200-201°.

Attempt to isomerize 2,9-dimethyl-4-ketodecahydroquinoline

A solution of 0.2 g of metallic sodium in 65 ml of methanol was added to 8 g of the base (II) (b.p. 99-100° at 3 mm; n_D^{20} 1.5021). The solution was boiled for 5 hours. After treatment as described above and distillation under reduced pressure, 7.3 g of the initial 2,9-dimethyl-4-ketodecahydroquinoline, with b.p. 100-101° at 3 mm; n_D^{20} 1.4997, was obtained. The picrate melted at 199-200°, and gave no depression with the picrate of the initial material.

1,2-Dimethyl-4-ketoperhydro-1-pyrindine (VI)

A solution of 50 g of β-methoxypropyl-Δ^1-cyclopentenylketone (IV) (b.p. 85-86° at 3 mm; n_D^{23} 1.4803 [3]) and 80 g of 25% aqueous methylamine in 60 ml of methanol was heated in a sealed metal tube for 5 hours at 70°. The methanol and excess methylamine were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral product extracted with ether. The reaction product was separated by the addition of solid alkali with ice-water cooling, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. 39 g of 1,2-dimethyl-4-ketoperhydro-1-piperindine (VI), with b.p. 88-89° at 2 mm; n_D^{24} 1.4922.

After heating the product (39 g) with 7% hydrochloric acid (125 ml) at 70-80° for 1 hour, 35.4 g of pure 1,2-dimethyl-4-ketoperhydro-1-pyrindine (VI) with b.p. 86-87° at 2 mm; n_D^{20} 1.4912; d_4^{20} 1.0104, was obtained. Found MR 47.94; calculated MR 47.93.

Found %: N 8.48, 8.56.
$C_{10}H_{17}ON$. Calculated %: N 8.37.

After recrystallization from ethanol the picrate melted at 164.5-165°.

An attempt to isomerize 1,2-dimethyl-4-ketoperhydro-1-pyrindine in methanolic sodium methoxide solution, as described above, afforded only the initial material, as shown by a melting point test of the mixed picrates.

2-Methyl-4-ketoperhydro-1-pyrindine (V)

A solution of 40 g of β-methoxypropyl-Δ^1-cyclopentenylketone (b.p. 85-86° at 3 mm; n_D^{20} 1.4803 [3]), and 100 g of 25% aqueous solution of ammonia in 75 ml of methanol was heated in a sealed metal tube for six hours at 60°. The methanol and excess ammonia were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral products extracted with ether. The base was separated by the addition of solid alkali with ice-water cooling, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. The yield was 27.2 g of 2-methyl-4-ketoperhydro-1-

pyrindine (V) with b.p. 85-86° at 1 mm; n_D^{20} 1.4982; d_4^{20} 1.0381; found MR 43.27; calculated MR 42.97.

Found %: N 9.13, 8.98.
$C_9H_{15}ON$. Calculated %: N 9.14.

The picrate after recrystallization from alcohol melted at 161-162°.

An attempt to isomerize 2-methyl-4-ketoperhydro-1-pyrindine by heating for 4 hours in methanolic sodium methoxide solution yielded only the initial material, as was proved by a mixed picrate melting point test.

1,2,6,7a-Tetramethyl-4-ketoperhydro-1-pyrindine (IX)

A solution of 25 g of a mixture of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) with its corresponding methoxyketone (b.p. 90-98° at 4 mm; $n_D^{22.5}$ 1.4795 [4]) and 45 g of 25% aqueous methylamine in 50 ml of methanol was heated in a sealed metal tube at 70° for 4 hours. The methanol and excess methylamine were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1: 1), and the neutral product extracted with ether; the base was carefully separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 17 g of 1,2,6,7a-tetramethyl-4-ketoperhydro-1-pyrindine (IX) with b.p. 94-97° at 4mm; n_D^{20} 1.4915, was obtained. Residue of resinous substance, 5.3 g.

When the 17 g of base (IX) thus obtained was heated with 45 g of 7% hydrochloric acid at 70-80° for one hour, 12.9 g of pure base (IX) with b.p. 90-92° at 4 mm was obtained; n_D^{20} 1.4894; d_4^{20} 0.9800; found MR 57.46; calculated MR 57.16.

Found %: N 7.01, 7.29.
$C_{12}H_{21}ON$. Calculated %: N 7.12.

The picrate, recrystallized from alcohol, melted at 184-185°.

An attempt to isomerize 1,2,6,7a-tetramethyl-4-ketoperhydro-1-pyrindine in methanolic sodium methoxide solution yielded only the initial material, as was shown by a mixed picrate melting point test.

2,6,7a-Trimethyl-4-ketoperhydro-1-pyrindine (VIII)

A solution of 22 g of a mixture of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) and the corresponding methoxyketone (b.p. 90-98° at 4 mm; n_D^{22} 1.4705 [4]) and 45 g of 25% aqueous ammonia in 75 ml of methanol was heated in a sealed metallic tube at 70° for 4 hours. The methanol and excess ammonia were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1: 1), the neutral products extracted with ether. The base was carefully separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 15.6 g of 2,6,7a-trimethyl-4-ketoperhydro-1-pyrindine (VIII) with b.p. 85-86° at 3.5 mm was obtained; n_D^{20} 1.4842; d_4^{20} 0.9849; found MR 52.64; calculated MR 52.21.

Found %: N 8.14, 7.94.
$C_{11}H_{19}ON$. Calculated %: N 7.72.

The picrate separated from an alcoholic solution after standing for several months, and after recrystallization from alcohol melted at 164.5-165.5°.

Cis-2-vinylethynyl-2-decalol

To 180 g of powdered potassium hydroxide and 1100 ml of dry ether in a round-bottomed flask a mixture of 315 g of cis-β-decalone (b.p. 113-114° at 14 mm; n_D^{20} 1.4910) and 200 g of vinylacetylene dissolved in 250 ml of dry ether was added with constant stirring and cooling to −10° over 3 hours. The reaction mixture was stirred and kept cool for 6 hours, and on the following day it was treated with water (250 ml). The product was extracted with ether, neutralized with 8% hydrochloric acid, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. A yield of 280 g of cis-2-vinylethynyl-2-decalol with b.p. 131-132° at 6 mm and n_D^{18} 1.5340 was obtained. Trans-2-vinylethynyl-2-decalol was obtained from trans-β-decalone and had b.p. 116-118° at 4 mm; n_D^{20} 1.5228 [6].

Cis-2-vinylethynyloctalin

A mixture of 280 g of cis-2-vinylethynyl-2-decalol and 280 g of 50% sulfuric acid was vigorously stirred at 60° for 8 hours. At the end of the reaction the hydrocarbon layer was separated, neutralized with sodium carbonate solution, dried over sodium sulfate, and distilled under reduced pressure. A yield of 160 g of cis-2-vinylethynyloctalin was obtained; it had b.p. 100-102° at 2 mm; n_D^{20} 1.5485. Trans-2-vinylethynyloctalin has b.p. 100-102° at 3 mm; n_D^{20} 1.5482 [6].

β-Methoxypropyl-2-octalylketone (X) or (Xa)

A mixture of 165 g of cis-2-vinylethynyloctalin, 3.5 g of concentrated sulfuric acid, 50 g of mercuric sulfate (added in three portions), and 1230 g of 95% methanol was stirred at 60° for 7 hours. The methanol was distilled off under reduced pressure, the product extracted with ether, neutralized with sodium carbonate solution, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 160.7 g of β-methoxypropyl-2-octalylketone (X) or (Xa) was obtained; it had b.p. 150-154° at 7 mm; n_D^{20} 1.5120.

Allyl-2-octalylketone

30 g of the bicyclic methoxyketone (X) or (Xa) and 0.1 g of p-toluenesulfonic acid were heated for 20 minutes under vacuum (130°, 100 mm). On distillation, 20 g of allyl-2-octalylketone with b.p. 133-135° at 3 mm was obtained; $n_D^{20.5}$ 1.5220. Allyl-2-octalylketone obtained from trans-β-decalone has b.p. 133.5-135° at 4.5 mm; n_D^{20} 1.5234 [6]. The product failed to crystallize on long standing at −75°.

1,2-Dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or XIIa)

A solution of 50 g of β-methoxypropyl-2-octalylketone (X) or (Xa) (b.p. 150-155° at 7 mm; n_D^{20} 1.5120) and 60.8 g of 25% aqueous solution of methylamine in 150 ml of methanol was heated in a sealed metal tube for 6 hours at 70°. The methanol and excess methylamine were distilled off under slightly reduced pressure; the residue was acidified with dilute hydrochloric acid (1:1), and the neutral product was extracted with ether. The reaction product was separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. A yield of 25.3 g of 1,2-dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or (XIIa) with b.p. 145-152° at 3mm was obtained; n_D^{19} 1.5221, and a resinous residue, 5.1 g.

When the product (25 g) was heated to 80° for one hour with 7% hydrochloric acid (60 ml), 20.6 g of the p pure base with b.p. 142-143° at 3mm was obtained; n_D^{20} 1.5210; d_4^{20} 1.0317; found MR 69.44; calculated MR 68.82.

Found %: N 5.56, 5.61.
$C_{15}H_{25}ON$. Calculated %: N 5.95.

The picrate separated as an oil. The picrolonate, when recrystallized from aqueous alcohol, melted at 201-203° with decomposition. Distillation of the neutralized reaction products yielded 13 g of the initial methoxyketone with b.p. 136-138° at 4 mm; n_D^{20} 1.5110.

2-Methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa).

A solution of 20 g of β-methoxypropyl-2-octalylketone (X) or (Xa) (b.p. 150-154° at 7 mm; n_D^{20} 1.5120) and 44 g of 25% aqueous ammonia in methanol was heated in a sealed metal tube for 5 hours at 70°. The methanol and excess ammonia were distilled off, the residue treated with dilute hydrochloric acid (1:1), and the neutral substances extracted with ether. The base was separated with alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. A yield of 9.6 g of 2-methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa) was obtained; it was a thick, colorless liquid with a typical amine odor: b.p. 140-142° at 2 mm; n_D^{20} 1.5196; d_4^{20} 1.0435; found MR 64.38; calculated MR 63.86.

Found %: N 6.47, 6.38.
$C_{14}H_{23}ON$. Calculated %: N 6.32.

The picrate failed to separate from alcoholic solution even after 4 months standing. Distillation of the neutral products yielded 4.7 g of the initial methoxyketone with b.p. 135-138° at 3 mm; n_D^{20} 1.5110.

SUMMARY

1. A number of polycyclic compounds, containing the 4-piperidone nucleus condensed with cyclohexane, cyclopentane, and decalin, have been synthesized. Some of the compounds obtained contain angular methyl groups.

2. It has been shown that the method developed in our laboratory for the synthesis of 4-piperidones from vinylallylketones and ammonia and primary amines is applicable to the preparation of the most diverse polycyclic compounds with condensed 4-piperidone nuclei.

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Academy of Sciences, USSR

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* See Consultants Bureau Translation, p. 2079 ff.

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ACETYLENE DERIVATIVES

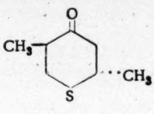
COMMUNICATION 152. HETEROCYCLIC COMPOUNDS.

XXVIII. THE SYNTHESIS OF SOME DERIVATIVES OF TETRAHYDRO-γ-THIOPYRONES

I. N. Nazarov and A. I. Kuznetsova

In a previous paper [1] we described a number of acids of the thiopyran series which were synthesized in order to determine their physiological activity. It also seemed of interest to prepare semicarbazones and thiosemicarbazones of the tetrahydro-γ-pyrones and their corresponding sulfones, since several thiosemicarbazones are known to have antitubercular activity [2,3].

By the interaction of trans-2,5-dimethyltetrahydro-1-thiopyran-4-one (I), which we have previously described [4] and its corresponding sulfone (II) with hydroxylamine sulfate in the presence of sodium acetate, the corresponding oximes (III) and (IV) were obtained in good yield.



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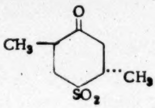

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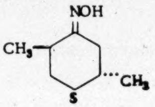

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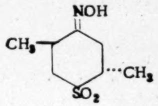
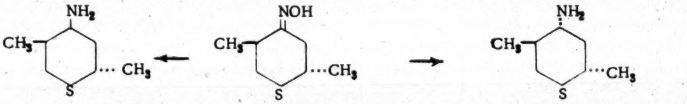


(IV)

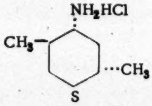
Reduction of the oxime (III) afforded two geometric isomers of the corresponding amine (V) and (VI)



(V) (III) (VI)

It is known that oximes of the cyclohexane and piperidine series [5] yield trans amines when they are reduced in alkaline media, but in acid media cis structures are produced. Reduction of the oxime (III) by metallic sodium in absolute alcohol afforded 2,5-dimethyltetrahydro-1-thiopyran-4-amine (VI) in 55% yield; by analogy with the cyclohexane and piperidine compounds this must have the trans structure.

When dry hydrogen chloride was passed through an alcoholic solution of the amine (VI), the amine hydrochloride (VII) was formed; in the same way, carbon dioxide gave the corresponding carbonate. On treatment with acetic anhydride the amine (VI) gave the acetyl derivative (VIII); with benzoyl chloride in pyridine it gave the benzoyl derivative (IX)



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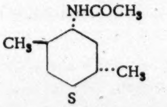

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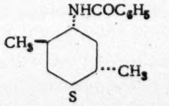
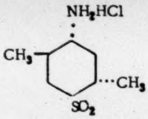


(IX)

On oxidation of the amine hydrochloride (VII) with 30% hydrogen peroxide solution in glacial acetic acid, the corresponding sulfone (X) was obtained; oxidation with 17% hydrogen peroxide in glacial acetic acid gave the the sulfoxide (XI). The sulfone (XII) was obtained by the interaction of the benzoyl derivative (IX) with 30% perhydrol solution in glacial acetic acid: (see top of following page).

Attempts to reduce the oxime (III) in neutral or acid medium in order to obtain the second possible stereoisomer of the amine (V) gave negative results. The catalytic hydrogenation of the oxime (III) could not be effected either in dioxan in the presence of Pd on calcium carbonate or in absolute alcohol saturated with hydrogen chloride in the presence of Pd on carbon. Reduction of the oxime (III) with the aid of zinc in alcohol



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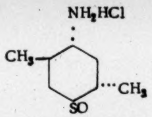

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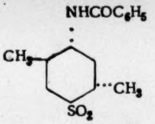
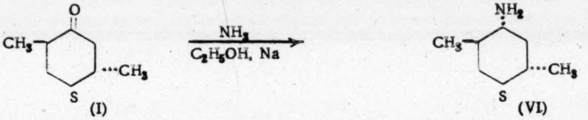


(XII)

solution saturated with hydrogen chloride, or with sodium amalgam in acetic acid solution afforded only traces of the amine (VI).

As is known, primary amines of the cyclohexane series are obtained in good yield by the catalytic hydrogenation of cyclohexanones in the presence of ammonia. Colloidal platinum [6] or Raney nickel [7] may be used as a catalyst. For some of the aliphatic ketones this reaction may be effected by the action of metallic sodium in alcoholic ammonia solution [8].

We attempted to use the method described above to prepare amines of the thiopyrone series. The action of metallic sodium on the thiopyrone (I) in alcoholic ammonia solution gave the amine (VI) as the hydrochloride in 14% yield:

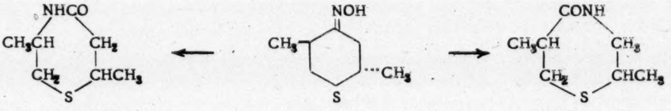


An attempt to hydrogenate the sulfone (II) in alcoholic solution of ammonia under normal pressure in the presence of Raney nickel gave only the unchanged starting material; the hydrogenation does not take place under these conditions.

Thus, by reduction of the oxime (III) and reduction of the thiopyrone (I) in ammonia solution, we only obtained one stereoisomer of the amine (VI).

The Beckmann rearrangement of ketoximes to substituted amides is well known and has been extensively studied in the aliphatic, aromatic, and heterocyclic series with the use of the most diverse reagents [9]. Rearrangement of the oximes of the cyclohexane series has been effected with sulfuric acid, phosphorus pentoxide, or benzenesulfonyl chloride [10], and has found practical use in the synthesis of artificial fibers.

However, the rearrangement of oximes of the thiopyran series has not yet been studied. As with the cyclohexane oximes, here also the formation of lactams of two thioaminoacids may take place in the following manner:

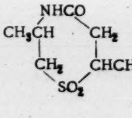


(XIII) (I) (XIV)

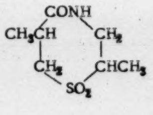
Heating of the oxime (I) with 70% sulfuric acid produced only one lactam (XIII) or (XIV). The use of 50% acid led to hydrolysis of the oxime, and more concentrated acids (80-90%) lowered the lactam yield.

Rearrangement of the oxime (I) did not take place in the present of p-toluenesulfonyl chloride either in pyridine or in 20% potassium hydroxide solution. Neither could the rearrangement be effected by the action of phosphorus pentachloride, acetyl chloride in acetic anhydride solution, or hydrogen chloride in acetic acid.

Oxidation of the lactam (XIII) or (XIV) by perhydrol in glacial acetic acid gave the corresponding sulfone (XV) or (XVI).

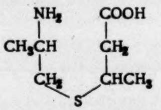


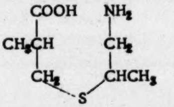
(XV)



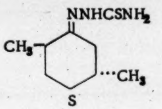
(XVI)

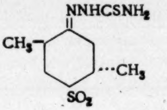
The lactam (XIII) or (XIV) was subjected to hydrolytic cleavage by boiling with hydrochloric acid and by treating the hydrochloride obtained, first with silver oxide and then with hydrogen sulfide, the acid (XVII) or (XVIII) was separated:

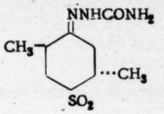

(XVII)


(XVIII)

In connection with the search for new medicinal preparations, it seemed of interest to prepare the thiosemicarbazones (XIX) and (XX), and also the semicarbazone (XXI), and to test them for antitubercular activity. These compounds were prepared by the usual method from the corresponding ketones:


(XIX)


(XX)


(XXI)

The compounds (III), (IV), (VII), (X), (XII), (XIX), (XX), and (XXI) were tested for antibacterial activity and found to be slightly active.

EXPERIMENTAL

The trans isomer of 2,4-dimethyltetrahydro-1-thiopyran-4-one (I) with m.p. 71° and its corresponding sulfone (II) with m.p. 138° [4] were used as starting materials.

2,5-Dimethyltetrahydro-1-thiopyran-4-one oxime (III). A mixture of 20 g of thiopyrone (I) dissolved in 20 ml of alcohol and a solution of 14 g of hydroxylamine sulfate with 17 g of sodium acetate in 40 ml of water was heated to 100° for 6 hours. On cooling, crystals separated; these were washed with water and recrystallized from alcohol. Yield 18.1 g of oxime (III) as colorless needles with m.p. 131-132°.

Found %: C 52.82, 52.63; H 8.23, 8.28; S 20.13, 20.14.
$C_7H_{13}ONS$. Calculated %: C 52.77; H 8.22; S 20.12.

Oxime of dihydroxy 2,5-dimethyltetrahydrothiopyran-4-one (IV). A mixture of a solution of 10 g of the sulfone (II) in 20 ml of alcohol and a solution of hydroxylamine sulfate with 4.5 g of sodium acetate in 20 ml of water was heated to 100° for 6 hours. The crystals which separated on the following day were collected and recrystallized from alcohol. Yield 7.15 g of oxime (IV) as colorless needles with m.p. 194-195°.

Found %: C 44.15, 43.96; H 6.81, 6.99; S 16.53, 16.98.
$C_7H_{13}O_3NS$. Calculated %: C 43.94; H 6.85; S 16.76.

2,5-Dimethyltetrahydro-1-thiopyran-4-amine (VI). To a solution of 5.8 g of the oxime (III) in 80 ml of absolute alcohol heated to 40°, 14 g of sodium, in small pieces, was added over 45 minutes with constant stirring. The cooled solution was diluted with water (80 ml) and thoroughly extracted with ether (100 ml). The ethereal solution was shaken three times with 10% sulfuric acid (75 ml in all). The aqueous-acid solution was concentrated to 25 ml and made alkaline with 20% sodium hydroxide solution. The free base was thoroughly extracted with ether and dried over potash. The ether was carefully distilled off in a flask fitted with a long spiral column, and the residue was then distilled in a current of nitrogen. A yield of 2.9 g of 2,5-dimethyltetrahydro-1-thiopyran-4-amine (VI) was obtained; it had b.p. 213°, and solidified to form colorless crystals with m.p. 37-40°.

Found %: C 57.55, 57.53; H 10.54, 10.66.
$C_7H_{15}NS$. Calculated %: C 57.85; H 10.40.

The amine (VI) was very soluble in most organic solvents and in water; it readily absorbed atmospheric carbon dioxide, forming the carbonate with m.p. 104-114°. The latter was stable when stored, but on heating it decomposed to give the original amine. When dry hydrogen chloride was passed through an alcoholic solution of the amine (VI), the subsequent addition of dry ether precipitated the hydrochloride (VII) as fine needles with m.p. 256-257°. The hydrochloride was stable in air and very soluble in water.

Found %: Cl 20.08, 19.80.
$C_7H_{15}NSCl$. Calculated %: Cl 19.51.

0.2 g of the amine (VI) and 0.5 g of acetic anhydride were set aside in a stoppered flask for 24 hours. The crystals of the acetyl derivative which formed (VIII) were recrystallized from benzene; they melted at 190-191°.

Found %: N 7.63, 7.59.
$C_9H_{17}ONS$. Calculated %: N 7.51.

5 g of the carbonate of the amine (VI) was dissolved by the aid of heat in 40 ml of dry pyridine. To the cooled solution 10 g of freshly distilled benzoyl chloride was added. Heat was evolved and a copious crystalline precipitate formed immediately. The crystals were filtered off, washed with weak sodium carbonate solution, and recrystallized from benzene. A yield of 4 g of the benzoyl derivative (IX) in the form of colorless crystals with m.p. 182-183° was obtained.

Found %: N 5.95, 6.08.
$C_{14}H_{19}ONS$. Calculated %: N 5.69.

Oxidation of 2,5-dimethyltetrahydro-1-thiopyran-4-amine hydrochloride (VII) with perhydrol. a) To a solution of 0.2 g of amine hydrochloride (VII) in 30 ml of glacial acetic acid, 2.8 ml of 30% perhydrol was added. After three days the bulk of the acetic acid was distilled off under reduced pressure. The precipitate was filtered off (0.25 g) and washed with ether. The aminosulfone hydrochloride (X) was purified by dissolving in alcohol and precipitating with ether, after which it melted at 285-286° (with decomposition).

Found %: N 6.71, 6.68.
$C_7H_{16}O_2NSCl$. Calculated %: N 6.58.

b) To a solution of amine hydrochloride (VII) in 75 ml of glacial acetic acid, 7 ml of 17% perhydrol solution was added. After four days the bulk of the acetic acid was distilled off under reduced pressure. The aminosulfoxide hydrochloride (XI) (0.5 g) was filtered off and after recrystallization from alcohol it melted at 330°.

Found %: N 7.24, 7.22.
$C_7H_{16}ONSCl$. Calculated %: N 7.07.

Oxidation of the amine benzoyl derivative (IX) with perhydrol. To a solution of 2 g of the benzoyl derivative (IX) in 40 ml of glacial acetic acid, 4 ml of 17% perhydrol was added. After three days the acetic acid was distilled off under reduced pressure, and after dilution with water the residue crystallized. A yield of 2 g of the sulfone (XII) was obtained; after recrystallization from alcohol it melted at 286-287°.

Found %; N 5.30, 5.45.
$C_{14}H_{14}O_3NS$. Calculated %: N 5.00.

Action of alcoholic ammonia and metallic sodium on the thiopyrone (I). To a solution of 5 g of thiopyrone (I) in 25 ml of 10% ammonia in absolute alcohol, 6.5 g of metallic sodium and 35 ml of absolute alcohol were gradually added, with stirring. After all the sodium had been dissolved 50 ml of water was added to the reaction mass, and the product was extracted with ether (100 ml). The ethereal solution was shaken with 10% hydrochloric acid (100 ml). The acid solution was evaporated to dryness and the salts obtained were dried in a vacuum desiccator and recrystallized by dissolving in water and precipitating with ether. A yield of 0.9 g (14% of the theoretical) of amine hydrochloride (VII) with m.p. 256-257° was obtained. A mixed melting point with the sample described above showed no depression. In addition 2.5 g of the initial thiopyrone (I) with m.p. 70-71° was obtained.

Rearrangement of the oxime (III) under the influence of sulfuric acid. 5.8 g of the oxime (III) and 9 ml of sulfuric acid were heated to boiling in a porcelain dish. The reaction mixture was cooled and gradually poured into 45 ml of 20% aqueous potassium hydroxide solution cooled with ice-water. The product was extracted with chloroform. The solvent was removed by distillation and the residue recrystallized from water with the addition of animal charcoal. A yield of 3.7 g of crystals of the lactam (XIII) or (XIV) with m.p. 139-142° was obtained. After three recrystallizations from water, 1.8 g of pure substance melting at 149-150° was separated:

Found %: C 52.90, 53.05; H 8.44, 8.43; S 20.07, 19.92.
$C_7H_{13}ONS$. Calculated %: C 52.77; H 8.22; S 20.12.

Oxidation of the lactam (XIII) or (XIV) with perhydrol. To a solution of 0.9 g of the lactam (XIII) or (XIV) in 5 ml of glacial acetic acid, 1.4 ml of 28% hydrogen peroxide solution was added. After three days the acetic acid was distilled off under reduced pressure and the residue recrystallized from alcohol. A yield of 1 g of sulfone (XV) or (XVI) as colorless needles with m.p. 221° was obtained.

Found %: C 44.04, 44.12; H 6.87, 7.09; S 16.98, 16.85.
$C_7H_{13}O_3NS$. Calculated %: C 43.95; H 6.85; S 16.77.

Hydrolysis of the lactam (XIII) or (XIV). A solution of 0.5 g of the lactam (XIII) or (XIV) in 2 ml of 10% hydrochloric acid was heated to 80° for one hour. The solution was evaporated under reduced pressure, and 2 ml of water was added to the residue after which the solution was again evaporated. 2 ml of water and 1 g of silver oxide were added to the residue. The precipitated silver chloride was filtered off and washed with water; the wash waters were treated with hydrogen sulfide. The separated silver sulfide was filtered off and thoroughly washed with water; the filtrate and wash waters were evaporated under reduced pressure. The glassy residue was dissolved in alcohol and precipitated with ether. A yield of 0.4 g of thioaminoacid (XVII) or (XVIII), as colorless crystals with m.p. 183-184° was obtained:

Found M: 185.2.
Calculated M: 177.33

Found %: C 45.91, 46.16; H 8.38, 8.51; S 17.94, 18.03.
$C_7H_{15}O_2NS$. Calculated %: C 47.42; H 8.53; S 18.09.

Thiosemicarbazone of 2,5-dimethyltetrahydro-1-thiopyran-4-one (XIX). Thiosemicarbazide (0.9 g) was dissolved with the aid of heat on the water bath in 30 ml of water and 2 ml of glacial acetic acid. To the hot semicarbazide solution 1.4 g of thiopyrone (I) dissolved in 25 ml of absolute alcohol was added. The precipitate of thiosemicarbazone (XIX) which formed immediately was recrystallized from alcohol and then melted at 162-163°.

Found %: N 19.30, 19.39.
$C_8H_{15}N_3S_2$. Calculated %: N 19.41

Thiosemicarbazone of dihydroxy 2,5-dimethyltetrahydro-1-thiopyran-4-one (XX). Thiosemicarbazide (0.9 g) was dissolved with heating on the water bath in 30 ml of water and 3 ml of glacial acetic acid. The slightly cooled solution was poured into a solution of 1.7 g of the sulfone (II) in 25 ml of absolute alcohol. The liquid was heated on the water bath for 15 minutes. The thiosemicarbazone (XX) melted at 241° (from water).

Found %: N 16.67, 16.58.
$C_8H_{15}O_2N_3S_2$. Calculated %: N 16.92.

Semicarbazone of dihydroxy 2,5-dimethyltetrahydro-1-thiopyran-4-one (XXI). The semicarbazone (XXI) was obtained from the sulfone (II) in the usual manner; it consisted of colorless needles melting at 217-218° (from water):

Found %: N 18.54, 18.40.
$C_8H_{15}O_3N_3S$. Calculated %: N 18.10.

SUMMARY

1. By the interaction of 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) and its corresponding sulfone (II) with hydroxylamine hydrochloride in alcoholic solution, the corresponding oximes (III) and (IV) were obtained.

2. Reduction of the oxime (III) with sodium in absolute alcohol afforded 2,5-dimethyltetrahydro-1-thiopyran-4-amine, which by analogy with compounds of the cyclohexane and piperidine series must have the trans-structure (VI). Attempts to prepare the second possible stereoisomer of the amine (V) by reducing the oxime (III) in an acid medium were not successful.

3. The same amine (VI) was obtained in 14% yield by the action of metallic sodium in alcoholic ammonia solution on the thiopyrone (I).

4. The hydrochloride (VII), the acetyl derivative (VIII), and the benzoyl derivative (IX) of the thiopyran amine, and also the hydrochloride (X) and the benzoyl derivative (XII) of the aminosulfone, and the hydrochloride of the aminosulfoxide (XI) have been prepared.

5. It is shown that the oxime of the tetrahydropyran series (III) rearranges to the lactam (XIII) or (XIV) on heating with sulfuric acid; hydrolytic cleavage of the lactam gave the thioamino acid (XVII) or (XVIII).

6. The thiosemicarbazones of 2,5-dimethyltetrahydro-1-thiopyran-4-one (XIX) and its corresponding sulfone (XX), and the semicarbazone of dihydroxy-2,5-dimethyltetrahydro-1-thiopyran-4-one (XXI) have been prepared.

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* See Consultants Bureau Translation, p. 897.

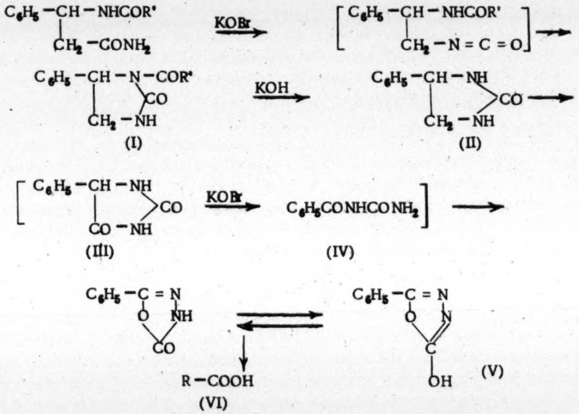
** See Consultants Bureau Translation, p. a-621.

NEW INFORMATION ON THE HOFMANN REACTION

COMMUNICATION 5. REACTION OF AMIDES OF N-ACYLATED β-PIPERONYL-β-ALANINES WITH ALKALINE HYPOBROMITES*

V.M. Rodionov and V.V. Kiseleva

In previous papers [1,2] we were able to show that the action of alkaline hypobromite solutions on amides of N-acylated β-phenyl-β-alanines proceeds in the following manner:



The substances (I) 1-N-acyl-5-phenylglyoxalidone, (II) 5-phenylglyoxalidone, (V) 5-phenyl-1,3,4-oxadiazol-2 (3H) - one and (VI) benzoic acid were separated from the reaction mixture, and the possibility of the formation of the substances (III) and (IV) (5-phenylhydantoin and acylurea) was shown in an indirect manner. Under the conditions of the Hofmann reaction, synthetically prepared phenylhydantoin and benzoylurea gave phenyloxadiazolone and benzoic acid. The mechanism given is a special case of a general mechanism for the reaction of hypobromites with amides of N-acylated β-aminoacids given by Rodionov and Zvorykina [3,4], where it is shown that in this reaction there is a difference in the further course of the process: 5-alkylglyoxalidones are oxidized to hydantoin derivatives and further, through α-ureidoacids to α-aminoacids; the alkyloxadiazolone could not be separated from the reaction mixture; 5-phenylglyoxalidone leads to the formation of 5-phenyloxadiazolone and benzoic acid through phenylhydantoin and benzoylurea which are not separated. Neither the α-ureido- or the α-aminoacid was separated from the alkaline medium.

In order to confirm the mechanism given on another representative of the β-aminoacids of the aromatic series, studies were carried out with amides of three acyl derivatives (benzoyl, acetyl and carbomethoxy) of β-piperonyl-β-alanine and it was shown that with these the reaction also proceeds by means of the mechanism given above; in all three cases 5-piperonylglyoxalidone (m.p.212-213°), 5-piperonyl-1,3,4-oxadiazol-2 (3H) -one (m.p. 242-243°) and piperonylic acid were separated; in the case of the benzoyl derivative, 1-N-benzoyl-5-piperonylglyoxalidone (m.p.255-256°) was also obtained. The latter gave no depression in a mixed melting point determination with 1-N-benzoyl-5-piperonylglyoxalidone (m.p. 241°) obtained by Rodionov and Bezinger [5] by carrying out the Curtius reaction on β-piperonyl-β-alanine.

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* Communications 4. see our paper in this journal, 1951, p. 57.

The reaction was carried out under the conditions we used previously in our work with β-phenyl-β-alanine (8 moles of alkali as a 13% solution and 2 moles of bromine per mole of amide; heating to 80°), and also under the somewhat milder conditions used by Rodionov and Zvorykina in work with β-aminopellargonic acid (7.6 moles of alkali and 2 moles of bromine per mole ofamide; heating to only 65°). In the latter case, 1-N-benzoyl-5-piperonylglyoxalidone was easily separated and piperonylic acid only with difficulty.

5-Piperonyl-1,3,4-oxadiazol-2(3H)-one and piperonylic acid were separated from the amide of N-carbomethoxy-β-piperonyl-β-alanine; from the amide of N-acetyl-β-piperonyl-β-alanine a substance with m.p. 265-266°, containing bromine and having the elementary composition $C_{12}H_{13}O_4N_2Br$ was obtained. The structure of this compound has not yet been established.

EXPERIMENTAL

β-Piperonyl-β-alanine was obtained in 40% yield by the method of Rodionov [6] in 50% yield by the method of Johnson [7], and in 60% yield by the method of Johnson as modified by Rodionov and Kravchenko [8]. N-benzoyl- β-piperonyl-β-alanine was prepared by the usual method, as already described by Bezinger [5].

N-Acetyl-β-piperonyl-β-alanine. To 5 g of β-piperonyl-β-alanine in 40 ml of 10% potassium hydroxide solution 4.1 g (3.85 ml) of acetic anhydride was added dropwise with constant mechanical stirring over 45 min. at 17-25°. At the end of the reaction a further 1.5 ml of 40% alkali was added (to make reaction alkaline). Stirring was continued for a further two hours and the solution was gradually acidified with dilute hydrochloric acid (1:1). The precipitate formed was filtered off, washed with cold water and dried. Yield, 6 g, m.p. 184-186° (quantitative yield); after recrystallization from hot water obtained in needles with m.p. 189-190°.

Found %: N 5.65; 5.65; $C_{12}H_{13}O_5N$. Calculated %: N 5.58.

N-Carbomethoxy- β-piperonyl-β-alanine. To a solution of 5 g of β-piperonyl-β-alanine in 10% potassium hydroxide solution (4g of solid KOH) 2.1 ml of methyl chloroformate was added dropwise at -2 to +2 with mechanical stirring (10% excess). Stirring was contined for a further hour and the solution was then acidified with hydrochloric acid (1:1). The oil which separated crystallized on standing overnight. Yield of N-carbomethoxy- β-alanine with m.p. 134-136°, 3.9 g (61% of theory); m.p. after recrystallization from ethanol 137-138°.

Found %: N 5.25; 5.13; $C_{12}H_{13}O_6N$. Calculated %: N 5.24.

Amide of N-benzoyl- β-piperonyl-β-alanine. Thirty grams of N-benzoyl-β-piperonyl-β-alanine and 13.6 ml of thionyl chloride (twofold quantity) were heated to 40° on the water-bath for 4 hours. Absolute ether was added to the oil formed and heating was continued for an hour and a half. The solidified mass was washed several times with absolute ether, the ether being decanted; on rubbing with a glass rod the whole mass crystallized under the ether; it was shaken up with fresh portions of ether and the suspension obtained was saturated with dry ammonia (the ether portions used for washing were saturated separately). The precipitate obtained was filtered off, washed with ether and dried in air; it was then washed four times with alkali and with water. On acidification the alkaline solution gave 0.2 g of the starting N-benzoyl derivative of β-piperonyl-β-alanine. Weight of solid amide, 25.5 g; m.p. 262-263°; after recrystallization from ethanol the m.p. was 267-268°. The amide was insoluble in hot water and slightly soluble in hot alcohol.

Found %: N 9.16; 9.31; $C_{17}H_{16}O_4N_2$. Calculated %: N 8.97.

The ethereal solution obtained in washing the reaction mass yielded a further 1.5 g of amide. Total yield of amide, 27 g (90% of theory).

Amide of N-acetyl- β-piperonyl-β-alanine. Twenty grams of N-acetyl-β-piperonyl-β-alanine and 17 ml of thionyl chloride (three times the theoretical quantity) were heated to 40° for two hours. Because the oil obtained was insoluble in both absolute benzene and absolute alcohol, it was treated several times with absolute ether, which was decanted. The solidified oil was rapidly rubbed in a mortar, shaken with ether and saturated with ammonia with frequent shaking (the ether from the washing was saturated separately). The solid was filtered off, dried in air, and washed with alkali and water. A yield of 14.8 g of amide with m.p. 200-201° was obtained; acidification of the alkaline solution gave 3.2 g of the starting N-acetyl-β-piperonyl-β-alanine. Yield of recrystallized amide, 88%. The amide was soluble in hot water and in hot alcohol. After two recrystallizations from hot water the m.p. was 213-214°.

Found %: N 11.20, 11.26; $C_{12}H_{14}O_4N_2$. Calculated %: N 11.20.

Amide of N-carbomethoxy-β-piperonyl-β-alanine. Twenty grams of N-carbomethoxy-β-piperonyl-β-alanine was heated with 10 ml of thionyl chloride (twice the theoretical) at 40° for two hours. The excess thionyl chloride was removed from the dark oil thus obtained by distillation under reduced pressure; and absolute ether was added to the oily residue. A suspension of the crystallized mass in ether was saturated with dry ammonia, with cooling and frequent shaking. The residue was filtered off, dried in air and washed three times with alkali and water. Yield of the recrystallized product with m.p. 212-216°, 16 g (~80% of theory). The amide was sparingly soluble in hot water and in hot alcohol. Yield of amide recrystallized from alcohol, 70%; m.p. 225-226°.

Found %: N 10.48; 10.62; $C_{12}H_{14}O_5N_2$. Calculated %: N 10.53.

The yield was lower when the theoretical amount of thionyl chloride was used.

Hofmann Reaction with the amide of N-benzoyl-β-piperonyl-β-alanine. (7.6 moles of KOH and 2 moles of bromine per mole of amide; heating to only 65°).

To 13% potassium hydroxide solution, containing 13.6 g of solid KOH, 3.3 ml of bromine was added at a temperature of −12-10°, and then 10 g of amide was added over two hours with stirring. The stirring was continued for a further hour in the cold and then for half-an-hour at room temperature The temperature of the bath was raised to 30°, when the amide dissolved completely. The heating was continued and at 50° the flask was removed from the bath, but the temperature inside the mixture rose spontaneously to 63°, while a solid separated and bubbles of gas were evolved. The flask was rapidly cooled, the precipitated solid filtered off and washed with acid, with water, with alkali and finally again with water. When made alkaline, the acid gave 0.2 g of a substance with m.p. 210-212° (I) and a residue of 4.3 g with m.p. 190-193° (II). The solution was extracted with ether during the extraction 0.3 g of the original amide separated. As a result of step-wise treatment of the solution with hydrochloric acid (1:1), two substances were separated:

Substance (III), 2.3 g; m.p. 183 to 215°.

Substance (IV), 2.05 g; m.p. 105-110°.

After purification of these four substances, the following were obtained:

1) 2.6 g of the starting amide,

2) 1.5 g of benzoic acid;

3) 0.1 g of N-benzoyl-β-piperonyl-β-alanine;

4) 2.4 g of 5-piperonylglyoxalidone (m.p. 212-213°).

Found %: C 58.26, 58.39; H 5.04, 4.97; N 13.36, 13.40. $C_{10}H_{10}O_3N_2$. Calculated %: C 58.25; H 4.85; N 13.59.

5) 0.3 g of 1-N-benzoyl-5-piperonylglyoxalidone - colorless needles with m.p. 255-256°; a mixed sample with the the original amide had m.p. 241-243°.

Found %: C 65.62; 65.76; H 4.70; 4.58; N 8.84; 8.87; $C_{17}H_{14}O_4N_2$ Calculated %: C 65.81; H 4.52; N 9.03.

6) 0.4 g of 5-piperonyl-1,3,4-oxadiazol-2(3H) -one - colorless needles with m.p. 243-244° (separted from other acids by treatment with bicarbonate).

Found %: C 52.43; 52.55; H 2.87; 2.93; N 13.62; 13.71; $C_9H_6O_4N_2$. Calculated %: C 52.43; H 2.91; N 13.59.

The structure of the 5-piperonyl-1,3,4-oxadiazol-2(3H) -one was confirmed by an alternative synthesis in which piperonylic acid hydrazide was treated with phosgene (method of Lieser and Nischk [9]. A mixed melting point on this product (m.p. 242-243°) and the product of the Hofmann reaction showed no depression.

Saponification of 1-N-benzoyl-5-piperonlyglyoxalidone. 1-N-benzoyl-5-piperonlyglyoxalidone (0.12 g) (m.p. 253-255°) was boiled for two hours on the water-bath with 20% KOH (with this treatment the turbid precipitate settled to the bottom and changed its form). After cooling, the solid was filtered off, washed with water and dried; 0.6 g of material with m.p., 208-209° was obtained, and a mixed melting point with 5-piperonylglyoxalidone gave no depression. On acidification and extraction with ether, the solution afforded 0.03 g of benzoic acid with m.p. 121-122°.

Hofmann Reaction with the amide of N-benzoyl-β-piperonyl-β-alanine under the earlier conditions. (8 moles of KOH 2 moles of bromine, heating to 80°).

This experiment differed from the preceding one in that after the temperature had increased the reaction mixture cooled and the solid separated, the solution was again heated to 55°. A further rise of temperature was observed;

the mixture was cooled and after separation of the precipitate, the solution was heated in two further steps: to 65 and to 80°. After removal of the precipitates, the solution was acidified as in the previous experiment. The products separated were worked up in the same way. The following were obtained from 10 g of amide:

1) 1.4 g of the original amide (m.p. 260°);
2) 1.2 g of pure 5-piperonylglyoxalidone (m.p. 212°)
3) 1.7 g of a mixture melting at 200-205° (not separated);
4) 0.08 g of 1-N-benzoyl-5-piperonylglyoxalidone (m.p. 253-255°).
5) 0.6 g of 5-piperonyl-1,3,4-oxadiazol-2(3H)-one (m.p. 242-243°).
6) 2 g of benzoic acid (m.p. 120-121°);
7) 0.05 g of piperonylic acid (m.p. 230°) and
8) 0.05 g of N-benzoyl-β-piperonyl-β-alanine (m.p. 195°).

Hofmann Reaction with the amide of N-acetyl-β-piperonyl-β-alanine (7.6 moles of KOH, 2 moles of bromine, heating to only 65°)

To a solution of hypobromite, cooled to −12° and containing 17 g of solid KOH, 113 ml of water and 4.08 ml of bromine, 10 g of amide (m.p. 213°) was added with stirring over an hour and a half. The solution was heated on the water-bath to 50°; the flask was then removed from the bath, when the temperature spontaneously rose to 65° and cloudiness developed. The flask was placed in a cooling-mixture; the precipitate (3.15 g) was found to be 5-piperonylglyoxalidone (m.p. 213°). The solution was then carefully acidified in the usual manner with hydrochloric acid (1:1) and the products separated were purified. From 10 g of amide the following were obtained:

1) 2.1 g of original amide (recovered);
2) 3.15 g of 5-piperonylglyoxalidone;
3) 0.7 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one;
4) 0.05 g of piperonylic acid and
5) 0.15 g of a bromine-containing substance having the elementary composition $C_{12}H_{13}O_4N_2Br$.
   Found %: C 43.78, 43.72; H 4.12, 4.04; N 8.31, 8.10. $C_{12}H_{13}O_4N_2Br$. Calculated %: C 43.77; H 3.95; N 8.51.

The examination of this substance has not yet been completed.

When the Hofmann reaction was carried out on N-acetyl-β-piperonyl-β-alanine with heating to 80°, the main reaction product obtained in three experiments was 5-piperonylglyoxalidone (yield 70-75%, based on the unrecrystallized product with m.p. 206-210°). In addition small amounts of 5-piperonyl-1,3,4-oxadiazol-2(3H)-one, N-acetyl-β-piperonyl-β-alanine and piperonylic acid were separated, as negligible quantities (0.03 g from 10 g of amide) of a bromine-containing compound, $C_{12}H_{13}O_4N_2Br$. The amide taken was entirely consumed in the reaction.

Hofmann Reaction with the amide of N-carbomethoxy-β-piperonyl-β-alanine.

This was carried out also under both mild and extreme conditions. From 10 g of amide the following were obtained:

Heating to 65°	Heating to 80°
3.5 g of original amide	0.1 g of originial amide
1.2 g of 5-piperonylglyoxalidone	4 g of pure 5-piperonylglyoxalidone (yield 51%; yield of technical product, 70%)
0.5 g of a mixture of 5-piperonylglyoxalidone and amide (m.p. 202-203°)	0.7 g of a mixture of 5-piperonyl-glyoxalidone and the amide
0.65 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one	1 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one
0.05 g of piperonylic acid	0.05 g of piperonylic acid

Subsequent experiments differed from the preceding ones in that the amide of the N-carbomethoxy derivative, which is difficult to wet, was first suspended in water and the hypobromite solution (calculated to make the alkali concentration 13%) was added dropwise to the suspension.

SUMMARY

1. The Hofmann Reaction has been carried out with the amides of N-benzoyl, N-acetyl and N-carbomethoxy- β-piperonyl-β-alanine under different conditions (heating to 65° and 80°).

2. It has been shown that in all cases the reaction mechanism is the same as that which occurs with the amides of of N-acylated β-phenyl-β-alanines. The mechanism may be considered a general one for amides of N-acylated aminoacids of the aromatic series.*

3. In all three cases 5-piperonylglyoxalidone, 5-piperonyl-1,3,4-oxadiazol-2(3H)-one and piperonylic acid were separated from the reaction-mixture; in addition the reaction with N-benzoyl-β-piperonyl-β-alanine yielded 1-N-benzoyl-5-piperonylglyoxalidone.

4. It has been shown that the separation of 1-N-benzoyl-5-piperonyglyoxalidone takes place readily under the conditions used by Rodionov and Zvorykina for amino-acids if the aliphatic series (heating to 65°), and the separation of piperonylic acid under the more drastic conditions (heating to 80°) which we have previously used (reaction proceeding further).

5. When the Hofmann Reaction was carried out on N-acetyl-β-piperonyl-β-alanine, a bromine-containing compound of composition $C_{12}H_{15}O_4N_2Br$ was separated.

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* The formation of 1-N-acyl-5-arylglyoxalidone and 5-arylglyoxalidone has already been confirmed for β-(α-naphthyl)-β-alanine by V.M. Rodionov and N. A. Kravchenko [8].

** See Consultants Bureau Translation, p. 847.

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STUDY OF THE REACTION MECHANISM OF CYCLIZATION WITH THE AID OF DEUTERIUM

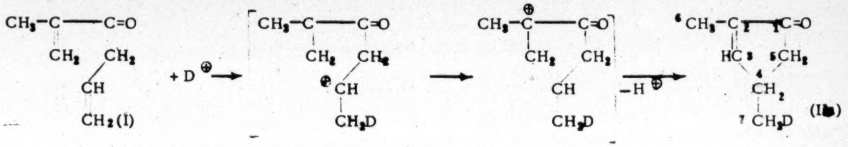
COMMUNICATION 2

I. N. Nazarov, I. I. Zaretskaya, Z. N. Parnes, and D. N. Kursanov

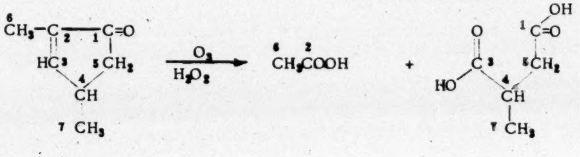
In a previous paper [1] we showed that the cyclization of 2-methylhexadien-3-one in the presence of deuterium-enriched phosphoric acid results in the introduction of deuterium into the molecule of dimethylcyclopentenone formed. From this observation it unambiguously follows that the cyclization reaction of this ketone proceeds by way of the intermolecular ionic mechanism proposed by Nazarov [2].

The aim of the present work was to determine the position into which the deuterium from deuterium-enriched phosphoric acid was introduced into the molecule of dimethylcyclopentenone formed. The determination of this position would make it possible to decide the question of the structure of the dienone entering this cyclization reaction. In order to solve this problem, we carried out the cyclization of 2-methylhexadien-3-one with the aid of deuterium-enriched phosphoric acid.

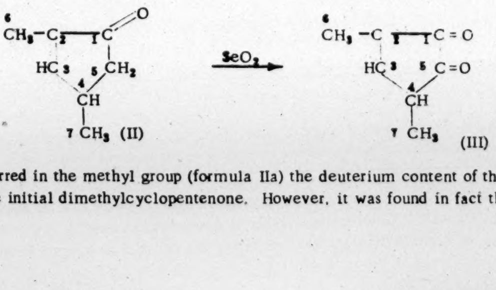
The combustion water thus obtained from dimethylcyclopentenone had an excess density equal to 2730 γ In this case, if the dienone entering the reaction had structure (I), then, as the scheme shown below demonstrates, the deuterium should be found at carbon 7.



In order to locate the deuterium, we ozonized the deuterium-containing dimethylcyclopentenone. As a result of this treatment and subsequent oxidation with hydrogen peroxide, methyl succinic acid was obtained having about the same amount of deuterium enrichment as the original dimethylcyclopentenone. On igniting this methyl succinic acid, water having an excess density of 2760 γ instead of the calculated 3410 γ was obtained. From this it follows that the deuterium could only be located at the carbon atoms 4, 5, or 7.

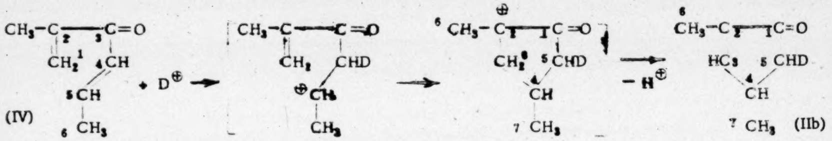


Further, the detuerium-containing dimethylcyclopentenone was subjected to oxidation with selenium dioxide. On oxidation of dimethylcyclopentenone, as was shown by Nazarov and Torgov [3], dimethylcyclopentendione is formed according to the following scheme:



If the deuterium occurred in the methyl group (formula IIa) the deuterium content of the diketone (III) should be the same as that of the initial dimethylcyclopentenone. However, it was found in fact that the diketone (III) contained practically no deuterium. The combustion water of the diketone (III) had a density excess of 94 γ instead of the calculated 3410 γ.[*] Thus it was shown that the oxidation of dimethylcyclopentenone (II) to dimethylcyclopentedione (III) is connected with the removal of deuterium.

Since the diketone (III) differs from the ketone (II) by the absence of hydrogen atoms at carbon 5, the absence of deuterium in the diketone (III) means that the deuterium in dimethylcyclopentenone is in the methyl group of carbon 5 (formula IIb). The fact that deuterium, as a result of the cyclization reaction, adds at carbon 5 may be explained only by supposing that the cyclization is actually undergone not by isopropenylallylketone (2-methyl-1,5-hexadien-3-one)(I), but by its isomer, 2-methyl-1,4-hexadien-3-one, (IV). In this case the reaction follows the following mechanism:



EXPERIMENTAL

Deuterodimethylcyclopentenone was obtained by cyclizing 2-methylhexadien-3-one with deuterium-enriched phosphoric acid. Before the experiments the dienone was distilled on a colum with a single glass-wound spiral having an efficiency of 25 theoretical plates and equipped with a manostat. The phosphoric acid was prepared from phosphoric anhydride and deuterium-enriched water containing about 50% of deuterium oxide.

Preparation of deutero-2,4-dimethyl-Δ^2-cyclopenten-1- one (IIb)

Experiment 1. In a 3-necked flask equipped with a stirrer, a dropping funnel and thermometer, 21.9 g of 2-methylhexadien-3-one (b.p. 68.5 -69.0° at 35 mm, $n_D^{20.4}$ 1.4732) was placed and phosphoric acid was gradually added with stirring and cooling by means of ice water. The phosphoric acid was obtained from 23.9 g of phosphoric anhydride and 7.8 g of deuterium-enriched water containing ~50% of deuterium oxide. During this operation the temperature in the reaction flask was maintained at 5-10°. After addition of phosphoric acid, the reaction mixture was stirred for a further 7 hours at 20°. The product was neutralized by sodium bicarbonate solution, extracted with ether, dried over sodium sulphate and, after removal of the ether, distilled under reduced pressure. Two fractions were obtained:

Fraction 1) b.p. 75-90° at 42 mm, 8.8 g.
Fraction 2) b.p. 90-100° at 42 mm, 2.1 g.

Fraction 1 was redistilled under diminished pressure and 6.5 g of ketone (IIb) with boiling point 75-76° at 30 mm; n_D^{20} 1.4670 was obtained. One gram of this substance was examined for deuterium. The water was burned in the usual laboratory apparatus and its density measured by the fusion method. The excess density of the combustion water was 2960 γ.

Experiment 2. 42.1 g of 2-methylhexadien-3-one (b.p. 57.5-58°) at 21 mm; n_D^{20} 1.4730) was subjected to the cyclization reaction in the presence of deuterium-enriched phosphoric acid obtained from 33.1 g of phosphoric anhydride and 16.3 g of water containing ~ 50% of deuterium oxide.

The reaction was carried out for 4 hours at 20° as described in the previous experiment. On distillation under reduced pressure at 11 mm the following fractions were obtained:

Fraction 1, b.p. to 57.0°; n_D^{22} 1.4660 – 0.4 g;
Fraction 2, b.p. 57.0-59.5°; n_D^{21} 1.4672 – 17.7 g;
Fraction 3, b.p. 60.0-83.0°; n_D^{21} 1.4642; – 4.3 g.

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[*] In order to find if the oxidation was accompanied by deuterium exchange, we carried out an oxidation experiment on light dimethylcyclopentenone with selenium dioxide in deuterium-containing acetic acid. It was found that the diketone obtained did not contain deuterium. This shows that there is no deuterium exchange under experimental conditions.

Fraction 2 consisted of dimethylcyclopentenone (II b). The excess density of the combustion water was 2730 γ (in the combustion 2.1 g of the dimethylcyclopentenone was used)

Ozonization of Deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one (IIb)

To a solution of 5 g deuterodimethylcyclopentenone obtained in Experiment 2, in 35 g of carbon tetrachloride, ozonized oxygen was passed for 8 hours at the rate of 3-4 litres per hour (ozone concentration 6%). The ozonized solution was poured into 25 ml of 5% hydrogen peroxide and mixed for 4 hours at 50°. The carbon tetrachloride and volatile acids were distilled off under slightly reduced pressure. The residue, in the form of a thick syrupy liquid, crystallized on cooling with an ice-salt mixture. The crystals (1.2 g) were filtered off and washed with cold ether, when they melted at 105-107°. After recrystallization from a benzene-light petroleum mixture, 0.4 g of crystals with m.p. 107-109° was obtained. The crystals were dried for four hours at a temperature of 70° under a pressure of 1 mm, after which they melted at 109-111° and gave no depression with a mixture of authentic methyl succinic acid. The volatile acids were neutralized with soda, the aqueous solution of salts evaporated to dryness and the salts treated with concentrated hydrochloric acid; the organic acids were all thoroughly extracted with ether. After the ether was distilled off, 1.2 g of acetic acid with b.p. 105-110° was obtained. The residue of 1.2 g crystallized. The crystals on filtering off and washing with cold ether melted at 107-109° and did not give a depression with an authentic specimen of methyl succinic acid.

The methyl succinic acid obtained as a result of recrystallization with m.p. 109-111° was examined for deuterium. It was found that the combustion water had an excess density of 2760 γ instead of the calculated 3410 γ. For the combustion 0.35 g of methyl succinic acid was used. Thus the methyl succinic acid contained almost all the deuterium taken for the ozonization of deuterodimethylcyclopentenone.

Oxidation of Deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one to 2,4-dimethyl-Δ^2-cyclopenten-1,5-dione (III)

5.5 g deuterodimethylcyclopentenone from Expt. 1, 7 g glacial acetic acid, and 5.7 g finely ground selenium dioxide were heated under an air condenser on Wood's alloy at 95-100°. An exothermic reaction set in and continued for 15 minutes. The mixture was heated to 115-120° for 15 minutes more, and after cooling was diluted with 30 ml ether, filtered, the acetic acid distilled off under slightly reduced pressure, and the residue distilled under the reduced pressure of an oil-pump. The substance obtained, 1.6 g with b.p. 80-85° at 3 mm, solidified to form a dense orange to yellow crystalline mass. Recrystallization from a mixture of petroleum ether and benzene afforded 0.9 g of dimethylcyclopentendione (III) as well-formed golden crystals with m.p. 64-65°.

The deuterium content of this diketone was measured. The excess density of the combustion water was 240 γ instead if the calculated 3700 γ. One gram of the compound was used in the combustion. As is evident from the results, the diketone contained practically no deuterium.

In another experiment 10 g of deuterodimethylcyclopentenone, obtained in experiment 2, was oxidized with 11.3 g of selenium dioxide and 18 g of glacial acetic acid. The reaction was carried out under similar conditions to those described above, and 3.6 g of crystalline diketone was obtained. After recrystallization from mixed petroleum ether and benzene, 1.4 g of pure dimethylcyclopentendione with m.p. 66-67.5° was obtained. The excess density of the combustion water from this diketone was found to be 94 γ instead of the calculated 3410 γ. For the combustion 0.85 g of the diketone was used.

In order to meet the objection that an exchange of hydrogen atoms between the ketone and glacial acetic acid might possible occur during the oxidation of dimethylcyclopentenone to dimethylocyclopentendione, we carried out an experiment to study the possibility of this exchange. Ordinary dimethylcyclopentenone was oxidized with selenium dioxide in glacial acetic acid containing deuterium. In the experiment 9 g of ketone, 11.0 g of selenium dioxide and 14.7 g of glacial acetic acid, enriched in the carboxyl group to the extent of 40,000 γ, were used. The experiment was carried out as described above. A yield of 2.4 g of diketone with mp. 67-68° was obtained. The combustion water from the diketone had an excess density of 30 γ instead of the calculated 3800 γ for 1H, and 11,870 γ for 8 H.

It may therefore be considered as proved that the deuterium in 2,4-dimethyl-Δ^2-cyclopenten-1-one is practically entirely in the methylene radical α to the carboxyl group. The experimental results are given in the Table.

Substance	Excess density of of combustion water in γ	No. of H atoms in the molecule	Degree of "heaviness".	
			in γ	in % of D content of dimethylcyclopentenone
Dimethylcyclopentenone	2960	10	29 600	100
Dimethylcyclopentendione	240	8	1 920	6
Dimethycyclopentenone	2730	10	27 300	100
Methylsuccinic acid	2760	8	22 080	81
Dimethylcyclopentendione	94	8	750	3

SUMMARY

1. Deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one was obtained by the cyclization of 2-methylhexadien-3-one in the presence of deuterium enriched phosphoric acid.

2. When deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one was ozonized, methylsuccinic acid was obtained which contained almost all the initial deuterium of the dimethylcyclopentenone. This excludes the presence of deuterium at carbon atoms 1,2,3 or 6 in the molecule of deutero-2,4-dimethyl- Δ^2-cyclopenten-1-one.

3. Oxidation of deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one with seleniumdioxide gave 2,4-dimethyl-cyclopenten-1,5-dione containing no deuterium. From this it follows that the deuterium in deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one occurs at carbon 5, i.e., at the methylene group adjacent to the carbonyl.

4. This position of deuterium in deutero-2,4-dimethyl- Δ^2-cyclopentenone shows that it is not isopropenylallylketone (2-methyl-1,5-hexadien-3-one) (I) but its isomer, 2-methyl-1,4-hexadien-3-one (IV) that is cyclized.

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* See Consultants Bureau Translation, p. 103.

** See Consultants Bureau Translation, p. a-211.

PROGRESS IN RESEARCH ON THE CHEMISTRY OF ALKALOIDS OF ANABASIS APHYLLA *

A.S. Sadykov

In 1929 Orekhov, in studying the Central Asian plant Anabasis aphylla discovered a new liquid alkaloid of the composition $C_{10}H_{14}N_2$ (isomer of nicotine) and called it anabasine. In cooperation with Menshikov [2] the structure of anabasine was elucidated (α-piperidyl-β-pyridine) and from the plant new alkaloids were separated: lupinine $C_{10}H_{19}NO$, aphillidine, $C_{15}H_{22}N_2O$, aphilline, $C_{15}H_{24}N_2O$, and "base Y".

Anabasine was the first alkaloid discovered in the Soviet Union and served as the beginning of a large amount of work carried out by Orekhov, Menshikov and their co-workers on the study of the native flora. Soon after the discovery of anabasine, it was established that it had valuable insecticidal properties, and its industrial production from the plant (A aphylla) in the form of anabasine sulfate was begun. Anabasine sulfate is widely used as an agent for combatting agricultural crop pests, especially those affecting the cotton plant.

One of the most important branches of the national economy of our Republic is cotton raising. The Stalin program for the further increase in cotton productivity in the Uzbek S.S.R., the main cotton base of our Union, stipulates an increase in the rate of growth of this branch of the agricultural industry hitherto unknown in world practice. The Directives of the 19th Congress of the Party on the 5th five-year Plan for the development of the U.S.S R. call for an increase in the value of the harvest of raw cotton by 55-65% and an increase in the productivity of cotton in the regions of Central Asia to 26-27 centners per hectare.

In the Directives of the 19th Party Congress it is prescribed "To stipulate an increase in production capacity for ammonia, sulfuric acid, synthetic rubber, synthetic alcohol, soda, mineral fertilizers, especially the granulated types, and chemical agents for combatting plant pests"** The 11th Congress of the Communist Party of Uzbekistan called on the scientific research institutes in the Republic to develop more effective methods for countering pests and diseases of the cotton plant.

With these problems in mind we have in recent years carried out work on the chemical study of different types of anabasis for the content of alklaoids and other substances. At the same time we have made an extensive study of the chemistry of alkaloids of Anabasis aphylla with the object of modifying their molecules to obtain various pharmaceutical chemicals.

In the present article we give the results obtained by the author and his co-workers working in the Department of Plant Chemistry of the Central Asian State University (S.A.G.U.) and in the Institute of Chemistry of the Academy of Sciences, Uzbek S S R.

There are about 30 species of anabasis in Central Asia. We have chemically examined [3] about ten species for their content of alkaloids, organic acids and other materials. As a result of work carried out in cooperation with the S.A.G.U. Ust-Urtsk expedition and especially with the Botanical Plant Institute of the Turkmenian Academy of Sciences [4, 5] considerable growths of A aphylla have been discovered in the region of the Central Turkmenian Canal and these were found to be richer in alkaloids than the plants from South Kazakhstan, which were being worked for anabasine sulfate. . This cooperative work showed that it was possible to utilize a new raw material in industry and enabled the resources for the production of anabasine sulfate to be enlarged.

A chemical study of the plant [2] showed that A.aphylla contains a considerable amount of alkaloids from 1.29 to 12% (according to the data of various authors). The product was separated into two fractions by fractional distillation under reduced pressure. A low-boiling fraction (boiling point 136 to 138° at 2 mm), amounts to ~85% of the starting-material and a high-boiling fraction (boiling point ~200° at 2 mm) to 2.15%. The low-boiling fraction was separated by benzoylation or nitrosation and, as well as anabasine, a crystalline alkaloids, lupinine, $C_{10}H_{19}NO$, was obtained. From the high-boiling alkaloids the authors, making use of their different basicities, separated the crystalline alkaloids aphilline $C_{15}H_{24}N_2O$, aphillidine, $C_{15}H_{22}N_2O$, and "base V".

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* Report to the combined session of the Division of Chemical Sciences, Academy of Sciences, U.S.S.R., and the Academy of Sciences, Uzbek. S.S.R., 15.10.1952, Tashkent.

** Directives of the 19th Party Congress on the 5th five-year Plan for the development of the U.S.S.R., in 1951 to 1955. Pravda Press, 1952, page 10.

Because anabasine has powerful pharmacological properties, it can be used directly as a therapeutic agent. However, it is known that several of its derivatives (N-methylanabasine) have interesting physiological properties. In view of this and bearing in mind the ready availability of anabasine and other alkaloids of A. aphylla, we carried out various chemical operations on the base.

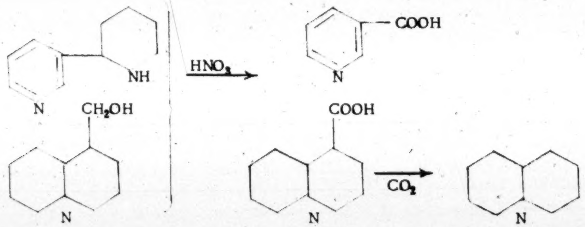
Before commencing this work it was necessary to develop methods for the separation of anabasine and other alkaloids of A. aphylla. For the separation of low-boiling alkaloids, apart from the methods of benzoylation and nitrosation mentioned above, other methods are used. Sokolov [6] proposed a fluosilicate method for the preparation of anabasine. Zaboev developed a new method in which nitrosation was carried out in acetic acid solution [7].

We have developed several new methods for separating anabasine or lupinine from mixtures of the two alkaloids [8]. Among these the hydrochloride method (formation of hydrochloride by the interaction of anabasine with hydrogen chloride or with ammonium chloride in acetone solution) is the simplest and the easiest and it may be recommended for the industrial preparation of pure anabasine. With a sufficient quantity of anabasine and the other alkaloids of A. aphylla at our disposal we were able to turn our attention to the chemical conversion of these bases.

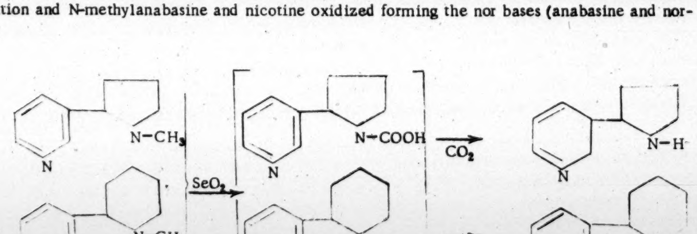
1. Oxidation of Anabasine.

As has been shown by Orekhov and Menshikov [2], when anabasine is oxidized with potassium permanganate, nicotinic acid is formed. This, apart from its use as the vitamin factor, is a raw material for a variety of further syntheses. We studied the oxidation of anabasine and its derivatives with different oxidizing agents in order to obtain nicotinic acid in large quantities for the needs of the medical institutions of our Republic.

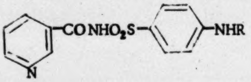
The oxidation of an anabasine-lupinine mixture with nitric acid [9] led to the formation of lupininic acid together with nicotinic acid. The former decarboxylizes with the formation of norlupinane:



The oxidation of cyclic and heterocyclic compounds has been studied by numerous workers. In review articles Melnikov [10] and Maior [11] have described numerous reactions of organic substances with selenium dioxide. Rodionov and his co-workers [12], studying the reaction in which cyclic and heterocyclic side chains are oxidized, developed an elegant and refined method for the preparation of the corresponding aldehydes. We [13] have oxidized anabasine, N-methylanabasine, and nicotine with selenium dioxide. Anabasine was found to be the most resistant to this oxidation and N-methylanabasine and nicotine oxidized forming the nor bases (anabasine and nornicotine):



In the literature there are many references to the synthesis of physiologically active compounds of nicotinic acid. We [14] have synthesized a number of new nicotinic acid derivatives mainly with several sulfanilamides. The general formula of the compounds obtained may be represented as follows:



Contrary to the findings of Daniels and Iwamoto [15], when sulfanilamide and nitotinyl chloride interact the main product is N-nicotinylsulfanilamide. Thus, by this synthesis we succeeded in solving the moot question in the literature on the addition of nicotinyl (the nicotinic acid residue) to the corresponding sulfanilamide group.

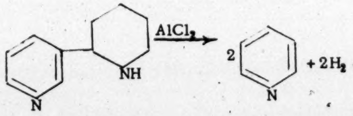
2. Fission of Anabasine

A number of workers have attempted to prepare pyridine from anabasine. Chelintsev and Dubinin [16] and later Aliev and Khanlarov [17] oxidized anabasine with nitric acid to nicotinic acid. By decarboxylation of the latter in the presence of a catalyst, pyridine was obtained. Dubinin and Chelintsev [18] subjected anabasine to pyrolysis on carbon at 580 to 600°. Pyridine was among the many products detected.

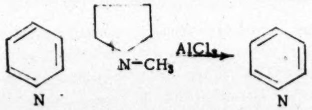
We have effected the fission of anabasine both thermally and by means of chemical reagents [19]. The thermal fission of anabasine (passing it through a heated quartz tube filled with activated clay or through an iron tube) yielded practically no pyridine. Of the chemical reagents for carrying out the fission of anabasine, zinc chloride, aluminum chloride, soda lime and metallic sodium were tried. We obtained good results with aluminum chloride and with metallic sodium.

It has been shown by various workers, especially by Zelinsky [20], that when aluminum chloride reacts with cyclic compounds the latter are dehydrogenated with the formation of various hydrocarbons.

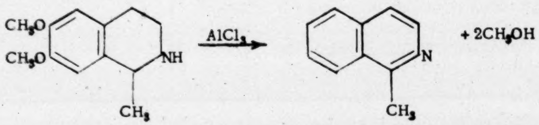
A series of reactions was carried out in which aluminum chloride acted directly on anabasine and on anabasine-lupinine mixtures. A yield of pyridine of 60-65% was obtained. The remainder of the anabasine was always recovered in the unchanged state. The absence of other reaction products prompted us to carry out some supplementary studies to establish the nature of the change of the piperidine nucleus in anabasine. Studying the reaction of piperidine with aluminum chloride under similar conditions, we were able to show that piperidine undergoes dehydrogenation with the almost quantitative formation of pyridine (yield 80-90%). Consequently, under the action of aluminum chloride the anabasine molecule suffers degradative fission at the $>C-\underset{\substack{|\\ H}}{C}<$ -bond with simultaneous dehydrogenation and the formation of two-pyridine molecules.



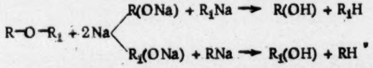
This was confirmed by subjecting nicotine to fission under similar conditions, when pyridine was obtained, but in a much smaller yield (12-15%). We were not able to observe in the reaction products even traces of pyrrole or pyrrolidine, since the latter under the reaction conditions evidently suffers profound changes.



The reaction of quinoline and of isoquinoline with aluminum chloride was then studied and it was shown that they are stable to this reagent. The alkaloid salsolidine (a derivative of tetrahydroisoquinoline) under these conditions gave 1-methylisoquinoline.



Metallic sodium was first proposed by Shorygin [21] for the cleavage of ethers and he proposed the following reaction mechanism:



$$R-O-R_1+2Na\begin{cases}R(ONa)+R_1Na\rightarrow R(OH)+R_1H\\ R_1(ONa)+RNa\rightarrow R_1(OH)+RH\end{cases}$$

However, we were not able to find in the literature any data relating to the cleaving action of metallic sodium on the $>C-CH<$ bond in heterocyclic compounds. When anabasine and metallic sodium were heated in molecular proportions (temperature 130-140°) destructive fission of anabasine takes place with the formation of pyridine (yield 70-75%). The pyridine formed was directly distilled from the reaction mixture. Thus, of chemical reagents, aluminum chloride and metallic sodium are recommended for the degradative fission of anabasine.

3. Ammination of Anabasine

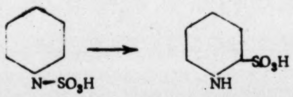
Soon after the structure of anabasine had been established, work was commenced on various derivatives of the latter and also on the study of the ammination reaction of anabasine and N-methyl-anabasine.

Orekhov and Norkin [24] and later Zhdanovich and Menshikov [25] synthesized a number of N-alkyl and N-aryl derivatives of anabasine. Menshikov, Grigorovich andOrekhov [26] and later Kabachnik and Katsnelson [27] made a detailed study of the ammination of anabasine and N-methyl anabasine in different solvents. In their work they showed that α and α_1 isomers are formed and they then proceeded to the synthesis of different compounds from the amminated products. Kabachnik and Zitser [28] in particular obtained acetylation products of N-methylamino-anabasines which are of definite interest pharmacologically. We have studied the ammination of anabasine and of N-methylanabasine under different conditions (without solvents, under pressure, without pressure and in the presence of different catalysts). As a result of this work we established the optimum conditions (temperature, proportions of reagents, effect of time and pressure) on the yield of reaction products, thus working out a comparativelysimple method for the synthesis of amminated derivatives of anabasine and N-methylanabasine. We proceeded to prepare various derivatives of the latter (sulfanilamide derivatives, acetylation and methylation products).

4. Sulfonation of Anabasine.

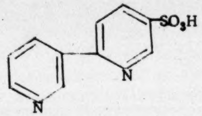
One section of the chemistry of anabasine which was studied was the sulfonation. The sulfonation of heterocyclic compounds has been the subject of many papers. Here we shall consider only the work of Terentyev and his school on the sulfonation of five-membered heterocyclic compounds [29]. It is known that these compounds are characterized by their high sensitivity to acids and therefore their sulfonation is often not possible with the usual sulfonating agents. For the sulfonation of similar compounds Terentyev successfully used pyridine sulfotrioxide, which had previously been used in the preparation of sulfamic acids (the sulfo group at the nitrogen). Terentyev and his co-workers obtained, in addition to the N-sulfamic acids, also various C-sulfonic acids of furan, thiophene, pyrrole, coumarone and indole.

We carried out the sulfonation of anabasine and its derivatives by means of pyridinesulfotrioxide in sulfuric acid The preparation of N-sulfamic acid of anabasine from pyridinesulfotrioxide was carried out by the method of Rubtsov [30] who used this reagent for the sulfonation of piperidine. As the author himself notes, he did not succeed in separating the N-sulfamic acid. Instead of this the 2-sulfo acid of piperidine was formed. When we sulfonated anabasine under these conditions we obtained the N-sulfamic acid, which was separated and characterized as the potassium salt. Attempts to prepare the C-sulfonic acid from the N-derivatives of anabasine (N-methyl, N-acetyl) gave negative results. In order to compare the behavior of the anabasine piperidine nucleus with piperidine, N-methyl and N-acetyl piperidine were sulfonated. In this case also we did not succeed in obtaining 2-piperidine sulfonic acid. From this it was possible to draw the conclusion that the secondary nitrogen is of a different character. The nitrogen of the piperidine nucleus in anabasine is more basic than that in piperidine and the formation of 2-piperidine sulfonic acid is connected with the isomerization of the sulfo group from nitrogen to the α-carbon atom.



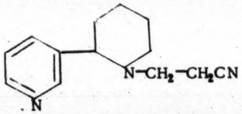
The sulfonation of anabasine by means of pyridine sulfotrioxide at 100-200° yielded no sulfonation products; at 200° isomerization of the pyridine sulfotrioxide to β pyridine sulfonic acid took place.

Sulfuric acid sulfonates anabasine at 300-320° with the formation of the monosulfonic acids of α-β-dipyridyl. The same acid was obtained when N-acetylanabasine was sulfonated. From an extensive study of the properties of the anabasine sulfonic acids and their conversion products, we were able to establish the structure of this compound.

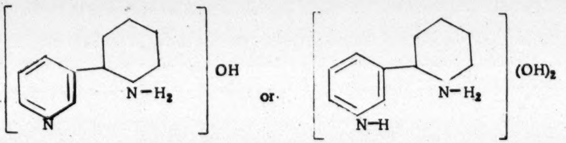


5. Cyanethylation of Anabasine

Over the past two or three decades many papers have appeared in the chemical literature dealing with the addition to acrylonitrile to the most diverse compounds, mainly organic, containing mobile hydrogen atoms. By means of this reaction, termed cyanethylation, β-substituted derivatives of propylnitrile and their conversion products became available. Many of the compounds obtained have an important practical value. We have studied the reaction between anabasine and acrylonitrile and ethylenecyanhydrin: N(β-propionitrile) anabasine has been prepared and characterized:



The effect of water on the rate of reaction between anabasine and acrylonitrile was studied. The cyanethylation reaction in aqueous solution has previously been described for ammonia and for a great number of aliphatic and alicyclic amines, but mainly in the presence of catalysts. Our experiments show that for anabasine the reaction with acrylonitrile without a catalyst proceeds at a moderate rate and only on heating. Water greatly increases the rate of this reaction. Anabasine is soluble in water with slight evolution of heat due to the partial formation of hydrates of the ammonium bases:



These ammonium bases, which are present in the reaction mixture, catalyze the addition reaction of anabasine to acrylonitrile by an ionic mechanism. This reaction mechanism which we have proposed has been confirmed by reactions in other solvents (e.g., petroleum ether). Quaternary ammonium bases (triton B, Rodionov's catalysts) have previously been proposed as additives to the cyanethylation reaction. When the reaction between acrylonitrile and anabasine in solvents was carried out in the presence of catalytic quantities of alkalies, quantitative yields of N(β-propionitrile) anabasine were obtained. This enabled us to work out a laboratory method for the separation of lupinine from mixtures with anabasine.

N(β-propionitrile) anabasine was used for further synthesis and conversions. When this was hydrolyzed with concentrated sulfuric acid N(β-propionamino) anabasine, N(β-aminoethyl) anabasine and N(β-carboxyethyl) anabasine were obtained. Hydrogenation of N(β-propionitrile) anabasine resulted in the separation of N(γ-aminopropyl)-anabasine and di[γ(N-anabasino)propyl]-amine. The following derivatives of N-(β-propionitrile) anabasine were obtained: N(γ-acetylamino)propyl)-anabasine, γ-N-anabasino propylethylurethane.

the ethyl ester of the γ-(N-anabasino)propylaminoacetic acid and N, N'-di[γ-(N-anabasino)-propyl]-urea.

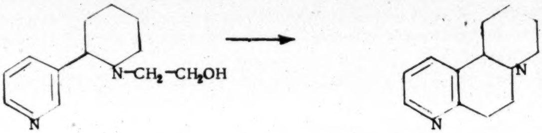
Thus, there are obtained ten new compounds as a result of the interaction of anabasine and acrylonitrile.

6. Reaction between Anabasine and Aliphatic Oxides

The work of many investigators, as well as our own, on the study of the alkaloids of plants, especially of A. aphylla at different vegetation stages has shown that the quantity of proportions of the different alkaloids in the plant is not constant. The question of the formation and the dynamics of accumulation of the alkaloids in the plant organism, as well as the part they play in the life process of the plant, has not been finally answered. It is also not entirely clear how alkaloids of one type of structure disappear during the course of the vegetation period with the formation of alkaloids of another structure with entirely different chemical structures.

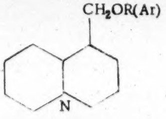
One method of studying the problem of alkaloid transition is to synthesize various intermediate compounds and to study the chemical conversion undergone by the alklaoids. This work, as well as being of great theoretical interest, has also practical value, since the intermediate products synthesized may possess physiological activity. Moreover, in studying changes in the structure of alkaloids it may be possible to find at what point new physiological properties make their appearance. For example, it is known that anabasine has insecticidal and other properties not possessed by other alkaloids. Thus, proceeding from anabasine to aphyllidine, or in the reverse direction, it may be possible to find when the new physiological properties appear.

One of the substances used for the preparation of these intermediate products in the study of A. aphylla alkaloids was the amino alcohol of anabasine which we had previously synthesized N(β-hydroxyethyl) anabasine. When this was dehydrated with phosphoric anhydride a crystalline base was obtained which possessed the systems of norlupinane and pyridine and which was termed 4,5-(α,β pyridylen)-norlupinane

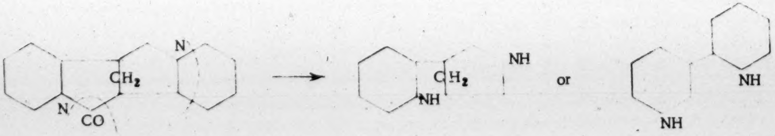


Work on the anabasine is also being carried out in other laboratories of our Republic. For example, we would mention the following: in the Institute of Chemistry of the Academy of Sciences Uzbek S.S.R. Talipov and co-workers [31] have studied the possibility of using anabasine in chemical analysis. Much work has been done on the study and synthesis of complex compounds of anabasine with salts of various metals by Udovenko, Azizov and co-workers [32]. In addition to anabasine we have also studied the secondary alkaloids of anabasine. Without going into details of the investigations of these alkaloids we may mention only a few results.

The methods which we worked out for the separation of anabasine-lupinine mixtures in particular with metallic sodium in hydrocarbons enables lupinine to be obtained in a satisfactory yield either as sodium lupinate or as the free base. Starting from sodium lupinate and chlorolupinane, we prepared a number of new compounds of the general formula [33]:



We have also studied the cleavage products of aphilline and aphillidine which are intermediate between the two structural types pachycarpine and α,β-dipiperidyl.



These investigations are directed toward finding several general methods for establishing the chemical nature of alkaloids of the C_{15} series (~30 of them are known). The importance of this work has greatly increased of late in connection with the use of aphilline as a substitute for novocaine.

The directives of the 19th Party Congress on the Five-year Plan for the Development of the USSR in 1951-55 stipulate a new increase in the development of science and technology.

"To improve the work of scientific research institutes and the scientific works of higher educational institutions, to fully utilize the scientific forces for the solution of important problems relating to the development of the national ecenomy for the dissemination of progressive knowledge and for the wide practical application of scientific discoveries;to cooperate with scientists in every possible way in the development of their theoretical problems in all branches of knowledge and to strengthen the connection between science and production." *

The mighty program for the development of the USSR outlined in the directives of the 19th Congress places great responsibility on the scientists of the Soviet Union. The work of the scientists of our Republic, and especially the chemists, must be directed toward the solution of the most important scientific problems connected with the development of industry, agriculture and especially cotton raising.

Institute of Chemistry
Academy of Sciences
Uzbekh SSR

Received 10 February 1953

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* Directives of the 19th Party Congress on the 5th Five-year Plan for the Development of the USSR in 1951-55. Pravda Press, 1952, page 29.

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* See Consultants Bureau Translation, p. 131.

THE REACTIONS OF ACETYLENE WITH AROMATIC COMPOUNDS*

I. P. Tsukervanik

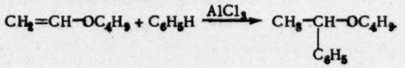
Acetylene has acquired great importance in modern synthetic chemistry. Thanks to the basic classical work of Kucherov, Favorsky, Zelinsky and many other Russian and Soviet chemists, various reactions of acetylene with inorganic and organic compounds are now widely used in industrial syntheses. In spite of the large amount of work on the chemistry of acetylene, several of its characteristics in known syntheses have not been studied up to now. In particular, the problem of the nature of the interaction of acetylene with aromatic compounds has not been solved; in other words, the problem of the alkylation of the aromatic nucleus by acetylene has not been elucidated. For comparison, it should be noted that in the case of ethylene and its homologs this alkylation has been well studied and is utilized on the industrial scale. We have selected this problem for treatment because it is closely connected with investigations of aromatic nuclear alkylation reactions on which we have been working for some time.

Acetylene, having a triple bond, may be considered as reacting in successive stages with rupture of the multiple bonds. In the first stage vinyl aromatic compounds should be obtained, and in the second, diarylethanes:

$$\begin{tikzcd} CH\equiv CH + ArH \arrow[r] & ArCH{=}CH_2 \arrow[d] & (1) \\ CH\equiv CH + 2ArH \arrow[r] & (Ar)_2CH{-}CH_3 & (2) \end{tikzcd}$$

Step-wise additions to acetylene are well known for many of its other reactions, and it would naturally be expected that the processes shown would be possible. Therefore, acetylene should be compared with bifunctional reagents (for example, with dihalogen derivatives, glycols, halogenhydrins, etc.), whose functional groups take part in alkylations either successively or simultaneously. The possibility of directing the reactions depends on the correct choice of conditions based on a study of the mutual influence of atoms and groups in the organic molecules entering into, and produced in, the synthesis.

In a number of previous papers [1, 2], we have shown that it is possible to direct the course of alkylation by bifunctional groups. The study of the condensation of benzene and anisole with vinyl ethers is closely related to the present problem [3]. In spite of the ease with which these ethers undergo polymerization and hydrolysis in the presence of aluminum chloride, conditions could be found under which the reaction took place at the double bond. α-Phenylethylbutyl ether was obtained from benzene:



$$CH_2{=}CH{-}OC_4H_9 + C_6H_5H \xrightarrow{AlCl_3} CH_3{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}OC_4H_9$$

We considered it necessary to dwell on these points in order to bring out the connection between the present problem and our other studies which cover much material of value in its solution. This introduction is also necessary because the unfounded and false view that it is impossible to add one molecule of benzene or a benzene derivative, to acetylene, has often been put forward in the literature. We have already given a detailed study of the relevant literature [4].

The possibility of effecting the practical alkylation of the benzene nucleus by acetylene is very good. Vinylbenzene is a most important raw material used in the manufacture of synthetic rubber and plastics. Several previous attempts in this direction gave negative results. Not only was vinylbenzene not obtained, but the diarylethanes were obtained in good yield only in isolated cases (ditolylethane). Either the condensation of acetylene with benzene did not proceed far, or else high-polymer insoluble resins, different from the ordinary polystyrenes, were obtained. Some authors, on the basis of their experimental work, consider that acetylene reacts at once only with two molecules of an aromatic compound [5]; others attempt to account for the formation of insoluble resins by suggesting a special intermediate vinyl compound ("protostyrene") [6]. It should be mentioned that in one of the older papers [7] it is reported that styrene was obtained as the main product of the condensation of benzene and acetylene. Later workers have not been able to confirm these results.

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* Paper read at a combined session of the Division of Chemical Sciences, Acad. Sci. U.S.S.R., and the Academy of Sciences, Uzbek. S.S.R., 25, X. 1952, Tashkent.

We commenced the study of the condensation of acetylene with benzene by showing the possibility of using different catalysts and the effect of different conditions on the course of the reaction. A large number of experiments were then carried out with toluene, naphthalene, anisole, chlorobenzene and dimethylaniline. The reactions were carried out not only with acetylene but also with vinyl chloride and with acetaldehyde. It was found that under the usual alkylation conditions, either insoluble resins (with active aluminum chloride at 60-80°), or small yields of diarylethanes (with moist aluminum chloride at 20°-40°) were obtained. In the reaction with benzene, in addition to 1,1-diphenylethane, the by-products ethylbenzene, 9,10-dimethylanthracene and a high-boiling resinous substance were produced. In this series of experiments our condensations with naphthalene, anisole and chorobenzene gave negative results [8].

In further benzene condensations, we used aluminum chloride containing various additives designed to reduce its activity. It was found that the addition of ferric chloride, and some other substances, increases the relative yield of low-boiling products (100-150°). Styrene was separated from these products and identified. In individual experiments the yield of styrene mounted to 15% of the total reaction product. In addition, distyrene was separated from the high-boiling fraction [9].

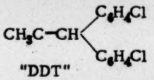
Thus, we showed that it was possible in principle to obtain aromatic vinyl compounds by the alkylation of acetylene. However, the total yield of products remained low. In order to raise the yield, it was necessary to carry out the condensation with active catalysts at high temperatures, at the same time avoiding the formation of insoluble resins. These resins are possibly polycondensation products of the diarylethanes. Korshak and his co-workers [10] have made a detailed study of the conditions and mechanism of formation of the aliphatic-aromatic polycondensation process. The condensation of benzene with dichloroethane with the formation of insoluble high-polymer resins similar in appearance to our resin is a reaction very closely related to our reactions. According to Korshak and his co-workers, an excess of dichloroethane is the main condition for the success of these polycondensations: with an excess of benzene, dibenzyl is formed. We established that 1,1-diphenylethane with an excess of dichloroethane also gives an insoluble resin. In studying afresh the condensation of dichloroethane with benzene, we found a number of supplementary conditions which promote high yields of dibenzyl.

Using these results we began to carry out the acetylene alkylations with the aromatic compounds in large excess and with reduced quantities of aluminum chloride at 40-60°. Under these conditions the insoluble resins were not formed at all, and the yields of the diarylethanes were greatly increased. 1,1-Diphenylethane was obtained in a yield of 55% of theory based on the acetylene consumed; chlorobenzene gave di-(p-chlorophenyl)-ethane in a yield exceeding 75% of theory; anisole gave dianisylethane in a yield of ~75%. In the latter case the possibility of using aluminum chloride activated with mercuric chloride was also shown [11]. The condensation of dimethylaniline with acetylene, acetaldehyde and vinyl chloride was studied in detail. Di-(p-dimethylaminophenyl)-ethane was obtained in a yield of up to 50% of theory. In this synthesis the possibility of the occurrence of an anomalous oxidative condensation leading to amino-derivatives of diphenylmethane and triphenylmethane was noted [12].

These condensation products with chlorobenzene, anisole and dimethylaniline are compounds which have been little studied. They had been obtained in these condensations only in traces. Further work in this direction will doubtless lead to an increase in the number of acetylene-alkylated aromatic compounds; obviously, an increase in the yield of the diarylethanes may also be achieved.

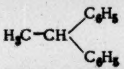
Thus, as a result of a study of the condensation of acetylene with organic compounds, we succeeded, in spite of data to the contrary in the literature, in carrying out the two reactions given in the equations above. We can speak of a new simple method for the synthesis of diarylethanes. On the other hand, we have every reason to affirm the possibility of synthesizing the aromatic vinyl compounds. The acetylene alkylation reaction can be directed in the same way as other similar reactions.

As well as studying different variants of the condensation, we began a systematic study of the diarylethanes for the purpose of utilizing them in various syntheses. We carried out the main reactions in which nuclear and side-chain hydrogen atoms are replaced —chlorination, nitration and sulfonation. Chlorination of the diarylethanes might lead to substances similar to a group of insecticides. The diarylethanes have the same carbon skeleton as "DDT". Both the chlorination and the nitration of the diarylethanes should therefore give a series of new substances with possible insecticidal properties:



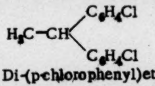
$$CH_3C-CH\left\langle\begin{matrix}C_6H_4Cl\\C_6H_4Cl\end{matrix}\right.$$

"DDT"



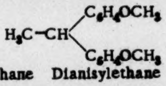
$$H_3C-CH\left\langle\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right.$$

1,2-Diphenylethane



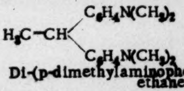
$$H_3C-CH\left\langle\begin{matrix}C_6H_4Cl\\C_6H_4Cl\end{matrix}\right.$$

Di-(p-chlorophenyl)ethane



$$H_3C-CH\left\langle\begin{matrix}C_6H_4OCH_3\\C_6H_4OCH_3\end{matrix}\right.$$

Dianisylethane



$$H_3C-CH\left\langle\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

Di-(p-dimethylaminophenyl) ethane

By chlorinating diphenylethane with heating and irradiation we obtained a high yield of the trichloroderivative, and on distillation this split off hydrogen chloride to give diphenyldichloroethylene. The composition and structure of the products have been shown by one of us [13].

$$(C_6H_5)_2CH-CH_3 \rightarrow (C_6H_5)_2CClCH_3 \rightarrow (C_6H_5)_2C=CCl_2.$$

On nitration, diphenylethane gave di-(p-nitrophenyl)-ethane [14] in 60% yield. On sulfonation, the p-disulfonic acid was obtained.

Finally, it is necessary to consider several general questions, connected with the working out of the problem. In the Directives of the XIX CPSU Congress the necessity of working out theoretical problems in all branches of knowledge is pointed out. In the field of organic chemistry, the basic theoretical problems were defined by the All-Union Conference on the Theory of Chemical Structure. In the Conference resolutions the following is placed among the problems regarded as of the first importance: "It is necessary that Soviet scientists should center their attention on deepening and extending our knowledge of the chemical structure of matter and on the development of the theory of the mutual influence of atoms in the molecule. It is necessary to work out problems on the dependence of molecular reactivity on structure and reaction medium."

It is just this problem which we have in mind in our work. Studies on the alkylation of aromatic compounds are still often limited by fixed views on the possibility of effecting and directing reactions. Meanwhile there is no doubt about the possibility of directing a synthesis in one direction or another on the basis of a knowledge of the characteristics of chemical structure and the effect of conditions. The study of a reaction direction which is difficult to bring about not only promotes the development of organic chemistry from the theoretical point of view, but also enables a number of practical tasks to be undertaken.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 54. ELEMENTARY REACTIONS OF THE POLYESTERIFICATION PROCESS

V. V. Korshak and S. V. Vinogradova

As a result of studies on the kinetics of the polycondensation process of hexamethylene glycol with sebacic acid, we showed that the mechanism of the process changes fundamentally in the different stages [1]. At first, when only the starting materials —hexamethylene glycol and sebacic acid —are present in the reaction mixture these interact. Water is thus eliminated and low-molecular-weight polyesters are formed giving a mixture which probably contains the following compounds:

$HO[CH_2]_6OOC(CH_2)_8COOH$ — acid ester of hexamethylene and sebacic acid,

$HO(CH_2)_6OOC(CH_2)_8COO(CH_2)_6OH$ — dihexamethyleneglycol ester of sebacic acid,

$HOOC(CH_2)_8COO(CH_2)_6OOC(CH_2)_8COOH$ —acid ester of hexamethyleneglycol and sebacic acid — hexamethylene-glycol disebacate, and

$H[O(CH_2)_6OOC(CH_2)_8CO]_2OH$ — the dimer.

After even half an hour the reaction mixture contained 60.9% of these low-molecular-weight polyesters, 33% of the starting-materials and only 6.1% of polyesters having a molecular weight higher than 900 (beginning with the trimer and higher). After 2.5 hours the amount of starting materials fell to ~ 4%, and the low-molecular-weight polyesters to 13.3%. However, the increase in molecular weight continued, from which it may be concluded, that the growth of the polyester molecule at this reaction stage is mainly due to the interaction of polyester molecules already formed.

Thus, the entire polyesterification process may be divided into two stages which differ sharply from one another in their reaction mechanisms: in the first stage the main reaction is between the starting materials, in the second the interaction of preformed polyester molecules predominates.

The low-molecular-weight monomeric starting materials react almost completely in the first stage of the process, and at the end of this the proportion of monomers present is so low that they play only a small part in the building up of polyester macromolecules.

However, their presence in small quantities is very necessary, because they play an essential part in catalyzing the process; in their absence the growth of polyester molecules is greatly retarded.

In the light of these results, it seemed of interest to study the separate elementary reactions of the polyesterification process, since it might be expected that their function and significance would differ in different stages. In the first stage of the polyesterification process, the main elementary reaction is obviously direct esterification, resulting from the interaction of alcohol and hydroxyl groups, and its mechanism may be established by studying the early stages of the polyesterification process, as has already been done by one of us in collaboration with Rafikov [2]. Therefore, in the present paper, we are concerned with finding if other possible reactions occur and with establishing their mechanisms.

We confined our studies to those intermediates which arise in the first reaction stage, and we investigated the diglycol ester of sebacic acid with the aim of finding out how it behaved under the polycondensation conditions and the possible routes of the conversions which it undergoes. The diethyleneglycol ester of sebacic acid was prepared by heating sebacic acid with an excess of ethylene glycol (recrystallized from benzene, melted at 60°). The diglycol ester thus obtained was heated under the conditions generally used in the polycondensation reaction at a temperature of 100 to 250°, under vacuum with a residual pressure of 1-2 mm. Tubes containing samples of the diglycol ester were heated for different times, varying from 1 to 30 hours and longer. Otherwise, the experimental methods were those previously described [3]. The product samples were extracted from the tubes and their molecular weights determined by the viscosity method in 0.5% benzene solution. Two experiments were carried out at each temperature — one without a catalyst, and the other with 0.5% of hydrated lithium oxide. The results obtained are given in Table 1.

TABLE 1

Polycondensation of Sebacic Acid Diglycol Ester

Heating time, in hours	Molecular weight of polyesters obtained at temperature of					
	100°		150°		200°	
	without catalyst	with catalyst	without catalyst	with catalyst	without catalyst	with catalyst
1	–	–	197	–	520	1823
2	197	524	–	–	1100	2835
3	–	–	–	–	1288	4050
4	–	–	317	768	–	–
5	317	786	–	–	–	5377
6	–	–	550	–	2746	–
7	–	–	–	1047	–	–
8	942	1042	–	–	4644	7500
9	–	–	1012	–	–	–
10	–	–	1047	1047	4644	8520
11	942	1012	–	–	–	–
12	–	–	1047	–	5000	9393
14	–	–	1047	–	–	10022
15	–	–	–	1047	–	–
16	–	–	–	–	–	10757
17	–	–	1047	–	6076	–
18	–	–	–	–	–	11069
20	–	–	1047	–	7927	–
24	–	–	–	–	–	12360
28	–	–	–	–	8100	–

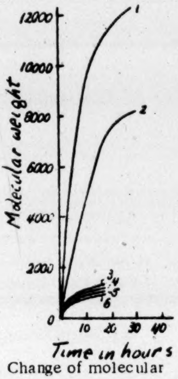

Fig. 1. Change of molecular weight with temperature: 1) Temperature 200° (cat.). 2) temperature 200° (without cat.); 3) temperature 150° (cat.); 4) temperature 100° (cat); 5) temperature 150° (without cat.); 6) temperature 100° (without cat.).

As will be seen from the results in Table 1, the molecular weight of the polyesters formed in the reaction increases with increasing temperature.. This relationship is especially clear in Fig. 1 which is based on the results of Table 1.

It should be mentioned that at a temperature of 200°; side-reactions, in which the polyester was decomposed, occurred; for this reason, the molecular weight values obtained at this temperature are not trustworthy.

Thus, it may be concluded that when the diglycol ester is heated polycondensation proceeds through a transesterification mechanism in which the hydroxyl groups of one molecule react with the ester links of another, as shown by the following equations:

$$\begin{aligned}&HOCH_2CH_2OOC(CH_2)_8CO\,OCH_2CH_2OH\\&+\\&HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OH \longrightarrow HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OOC(CH_2)_8\text{-}\\&\text{-}COOCH_2CH_2OH + HOCH_2CH_2OH\end{aligned}$$

The total polycondensation reaction may be expressed in the following form:

$$x\,HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OH \longrightarrow (x-1)HOCH_2CH_2OH + H[OCH_2CH_2OOC(CH_2)_8CO-]_x\,OCH_2CH_2OH$$

As will be seen from these equations, the polycondensation proceeds with the simultaneous separation of glycol, which is removed from the reaction sphere, and this promotes the process in which the polyester molecules are enlarged. Therefore, this case is another in which we have an equilibrium exchange reaction, the position of equilibrium depending on the rate of removal of the low-molecular-weight reaction products, as in other examples of polycondensation [4].

We have previously studied the kinetics of the transesterification reaction of esters with alcohol [5]. Ethyl stearate and cetyl alcohol were used and the studies were carried out at 122, 168, 183, and 250°, both with and without catalysts; the catalyst used was 1% of either sulfuric acid or sodium cetylate. It was found that the reaction rate and the extent of conversion increase with increasing temperature. The activation energy of the reaction at 170° was 12,950 cal/mole and the temperature coefficient, 1.34. This reaction was very sensitive to catalysts, the presence of which caused a marked increase in the rate. Thus, at a temperature of 183° without a catalyst the conversion reached 12.2%, while in the presence of sodium cetylate it amounted to 35%, and with sulfuric acid, to 61.5%. At lower temperatures, no reaction at all took place, but with increase in temperature the degree of conversion constantly increased. Thus, at 250°, the conversion was 36.3%, without a catalyst, and 66.6% with sodium cetylate. These results obtained with low-molecular-weight compounds such as ethyl stearate and cetyl alcohol [5] may be used in examining the polycondensation reaction of sebacic acid diglycol ester, since the mechanism of both processes is evidently the same. Moreover, a comparison of the results obtained in studies of both reactions shows their great similarity.

It was of interest to study the growth process of the macromolecular chains in this reaction, in order to compare it with the glycol and acid polycondensations which we have studied previously [1]. For this purpose, samples of sebacic acid diglycol ester were heated in tubes at a temperature of 200° and a residual pressure of 1-2 mm. After the heating, which was carried out for varios times, the content of free hydroxyl groups in the reaction product was determined; and the low-molecular-weight polyester fraction was separated from the high-molecular-weight fraction by extracting the product with a mixture of petrol ether and ethanol (4.5:5.5) for two hours with regular shaking. Control experiments showed that this solvent dissolves polyesters having molecular weights up to 900. The polyesters could thus be separated into two parts: a high-molecular-weight fraction of esters of molecular weight above 900, and a low-molecular-weight fraction of molecular weight less than 900. The results obtained are shown in Table 2.

TABLE 2

Heating time in hours	No. of ml of 0.02 N sodium hydroxide required in titration of hydroxyl groups in 1 g of polyester	% of High-molecular weight-polyester	% of Low-molecular weight polyester	Molecular weight Of high-molecular-weight polyester as shown by viscosity	Molecular weight Of low-molecular-weight polyester by end-group method.
0.0	334.8	0.0	100.0	–	–
0.7	213.0	2.1	97.9	997	847
2.0	97.5	24.9	75.1	1576	1449
3.0	92.5	55.9	44.1	1664	1538
6.0	41.9	91.8	8.1	2926	2857
9.0	23.8	98.2	1.8	4722	4545
12.0	21.7	98.3	1.7	5084	5000
17.0	18.0	98.3	1.7	6153	6060

The results of Table 2 show that the polycondensation of the diglycol ester proceeds in such a manner that at first a low-moleculcar-weight polyester is the main product, which is then converted to a high-molecular-weight form. This is made particularly clear in Fig. 2, which is based on the results in Table 2.

From a comparison of curve 4, showing the variation of low-molecular-weight polyester content of the reaction mixture, with curve 3, showing the variation in the hydroxyl group content, it may be seen that a rapid reduction in the content of hydroxyl groups is followed by a sharper fall in the proportion of low-molecular-weight-polyester. This is evidently explained by the initial separation of a large quantity of ethyleneglycol, but in the later stages of the reaction, when longer chains are reacting, this process takes place to a considerably lesser extent. The curve for the proportion of high-molecular-weight polyester, 2, rises rapidly in the first six hours, and changes only slowly, while the curve for molecular weight increases, 1, continues to rise. From this it may be concluded that the further increase in molecular size is due, not to the monomer of which little remains, or to

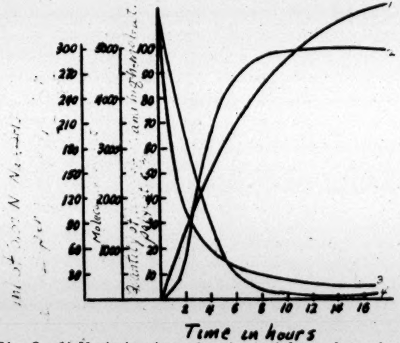

Fig. 2. 1) Variation in molecular weight as shown by viscosity. 2) variation in amount of high-molecular-weight polyester; 3) variation in amount of 0.02 N NaOH in cc. for titration of hydroxyl groups in 1 g of polyester. 4) variation in amount of low-molecular-weight polyester.

the low-molecular-weight polyesters leads to the formation of high-molecular-weight polyester molecules.

The picture observed in the case of the diglycol ester polycondensation is thus very similar to that which is observed in the polycondensation of glycol with a dicarboxylic acid, which we have already described [1]. This great similarity in the course of the formation of polyesters from these different starting materials suggests that it is the result of deep-seated causes. Evidently, it may be supposed that in the polycondensation reaction of glycols with dicarboxylic acids the increase in molecular size in the second stage of the process proceeds by way of a transesterification reaction, similar to that which occurs in the polycondensation of the diglycol ester, and not directly by the interaction of terminal hydroxyl and carboxyl groups, the concentration of which has become very low at this stage.

SUMMARY

1. The elementary reactions of the polyesterification process have been examined and it has been shown that the increase in molecular size at different reaction stages is due to different mechanisms.

2. The polycondensation of sebacic acid diglycol ester has been studied.

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MACROMOLECULAR COMPOUNDS.° COMMUNICATION 57.

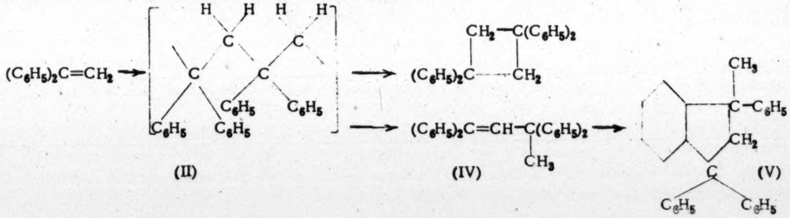
THE RELATION BETWEEN THE POLYMERIZATION CAPACITY AND THE STRUCTURE OF SOME UNSYMMETRICAL DIARYLETHYLENES

V. V. Korshak and N. G. Matveeva

In a previous paper we examined the question of the effect of stereochemical factors on the polymerization capacity of halogen-substituted ethylenes [1]. As a result of this investigation it was shown that steric hindrance to polymerization arises when the substituted ethylene molecule contains a large number of substituents of considerable size [2].

It was found that in the case of the halogen-substituted ethylenes, steric hindrance occurs only when three or four substituents are present, or with two when these are symetrically disposed. If the two halogen atoms are unsymmetrically disposed in relation to the double bond, then their screening effect is not great enough to interfere with polymerization, and for this reason all compounds of this type, such as vinylidene fluoride, chloride, bromide and iodide, polymerize very easily [1].

Still earlier, one of us in collaboration with Samplavskaya, suggested an explanation for the fact, which was observed by Lebedev [3], Belov [4] and other workers, [5], that unsymmetrical diphenylethylene, which also has only two substituents, forms only the dimer and gives no polymer [5]. In this case the cause of the early termination of the polymerization reaction may be seen in the development of strong steric strains in the molecule of the intermediate which is formed by the union of two monomer molecules. The reaction scheme previously put forward for the dimerization of 1,1-diphenylethylene is given below [5]:

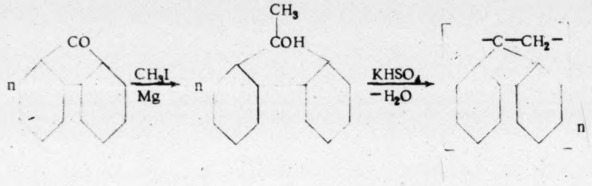


Thus, the first reaction stage consists of the formation of a biradical dimer (II). Like all free radicals which are intermediates in radical polymerization reactions, this intermediate is extremely reactive and unstable. Unusually, in the case of other polymerized compounds the reacton goes further, a third, fourth, etc., molecule adding to the type (II) product to give finally a long high-polymer chain. Because of stereochemical factors, such a process does not occur in this case. The large volume of the phenyl groups at the 1 and 3 carbon atoms, precludes the possibility of the usual zig-zag arrangement of carbon atoms, as shown in the scheme for product (II), and forces them into an arrangement in which either the molecule is planar forming a butane ring or the valence angles become deflected and the molecule is isomerized to the stable structure 1,1,3,3-tetraphenyl-butene-1(IV), which easily isomerizes to 1,1,3-triphenyl-3-methylhydrindene (V). It is easy to see that the cause of these strong steric stresses must be the phenyl groups, if the large volume which these occupy is considered; this is clear from Fig. 1 which represents a stereochemical model of 1,1-diphenylethylene.

That the dimerization of unsymmetrical diphenylethylene is due to effects of a stereochemical kind, and not to other causes, is clear from a comparison of the properties of this compound with those of isobutylene, the polymerization of which was studied by Butlerov as long ago as 1873 [6]. It is well-known that in the presence of ionic catalysts at low temperatures, isobutylene gives a very high-molecular-weight polymer [7]. An increase in the volume of even one of the substituents makes a fundamental change in the polymerization capacity. Thus, α-methylstyrene, because of the large volume of one of the substituents, fails to undergo radical polymerization when subjected to the action of heat, light or peroxides; but it is capable of forming a polymer under the influence of ionic catalysts, which are more active and better able to overcome steric hindrance than are the initiators of radical polymerization, as we have already shown [8]. In this connection, it seemed of interest to examine the problem of how changes in the position or structure of substituents affected the polymerization capacity of diphenylethylene.

There are references in the literature which indicate that diphenylethylene polymerizes on heating [9]. However, the polymerization conditions and the properties of the polymer have not been described in detail, and therefore, a study of this compound seemed of definite interest.

We prepared diphenylethylene by dehydrating 9-methylfluorenol, which was obtained from fluorenone and methylmagnesium iodide by the following reactions:



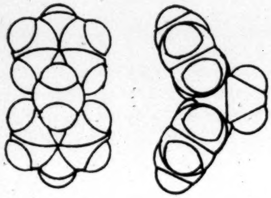


Fig. 1. Stereochemical model of the 1,1-di-phenylethylene molecule

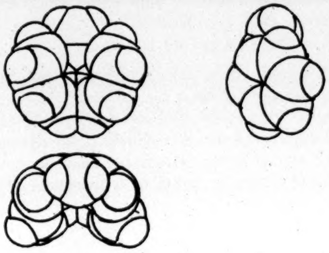


Fig. 2. Stereochemical model of the diphenylenethylene molecule.

Diphenylenethylene, formed by the dehydration of 9-methylfluorenone, polymerizes at once, and in none of our experiments were we able to separate the monomer. After reprecipitation, the diphenylenethylene polymer was obtained as a white powder, very soluble in benzene and in toluene but insoluble in alcohol, ether and water. The polyphenylenethylene softened at a temperature of 155-165°.

Thus, in spite of their great structural similarity, diphenylenethylene and 1,1-diphenylethylene differ in their tendency to polymerize; this is difficult to understand at first glance. If we examine the stereochemical model of diphenylenethylene shown in Fig. 2, and compare it with the molecule of 1,1-diphenylethylene in Fig. 1, the vast difference in the structure of these compounds becomes apparent at once.

In 1,1-diphenylethylene both the phenyl groups are entirely free and can easily rotate, and for this reason the space they occupy is greatly increased; but in diphenylenethylene, because of the presence of a bond between the phenyl groups, these are very compactly arranged and are not capable of free rotation round the ethylene carbon-carbon bond; they therefore do not cause steric hindrance to the same extent as we find in 1,1-diphenylethylene.

It should be added that in 1,1-diphenylethylene the phenyl groups have a strong screening effect on the ethylene carbon atoms which play an active part in the polymerization; these are prevented from touching, but the steric strains produced in the dimer molecule as a result of the mutual repulsion of the phenyl groups lead to isomerization of the biradical finally causing rupture of the chains of the growing molecule at the dimer stage, as shown in the reaction scheme (p. 487).

On the other hand, the phenyl groups in diphenylenethylene are so placed that the carbon atoms between which new bonds are formed in polymerization are easily accessible, and there is nothing to hinder the increase in chain length with the formation of a high-molecular-weight product. Here there is evidently no marked screening effect which might hinder the diphenylenethylene polymerization.

EXPERIMENTAL

Fluorenone

Forty grams of fluorene and 80 ml of acetic acid were placed in a flask fitted with a reflux condenser and a dropping-funnel and heated to gentle boiling [10]. A solution containing 135 g of potassium dichromate in a hot mixture of 160 ml of acetic acid and 40 ml of water was slowly added. During the dichromate addition the heating was stopped, since the heat of reaction caused the mixture to boil. When all the dichromate had been added boiling was continued for a further 3 hours. The reaction mixture was then poured into ice-water and set aside for 3 hours, after which it was filtered through cloth; the residue was washed, at first with dilute sulfuric acid and then several times with water, and dried in air.

The air-dried fluorenone was placed in a Claisen flask and distilled into a Würtz flask until a bright orange oil appeared. To remove fluorene, the fluorenone was dissolved in benzene (about 1 ml per gram) and the solution poured into twice its volume of petroleum ether. The fluorenone which was precipitated in large crystals was collected at the pump. The yield was 33.7 g or 73% of theory. The fluorenone melted at 83-84°.

9-Methylfluorenol

Methylmagnesium iodide was prepared from 2.4 g magnesium, and 14.2 g of methyl iodide in 50 ml of absolute ether [11] in a flask fitted with a reflux condenser and a dropping funnel. A solution of 18 g of fluorenone in 50 ml of ether was added with cooling to the methylmagnesium iodide. After all the fluorenone solution had been added, a few lumps of ice were placed in the flask and the reaction mixture was poured into dilute sulfuric acid. The ethereal layer was removed, washed several times with water and dried over sodium sulfate; the ether was then distilled off. The residue was recrystallized from benzene. Yield 10.3 g, i.e. 52.5% of theory.

9-Methylfluorenol consisted of white crystals melting at 176-177°.

Polydiphenylenethylene

9-Methylfluorenol (9.8 g) was placed in a flask and heated to 160-170° after 1 g of ignited potassium bisulfate and a little hydroquinone had been added. The solid polymer formed, was dissolved in benzene, washed with water, dried over sodium sulfate and precipitated by pouring the solution into excess of methanol. Polydiphenylethylene consisted of a white powder, melting at 155-165°; very soluble in benzene and in toluene and insoluble in alcohol, ether and water. Yield 53.03% of theory. Molecular weight by viscosity in benzene solution, 4890.

Found %: C 93.80; 93.50; H 6.07; 6.08
$C_{14}H_{10}$ Calculated %: C 94.34; H 5.65

SUMMARY

1. The absence of steric hindrance to polymerization in diphenylenethylene is explained on the basis of the compact arrangement of the phenyl groups in the molecule.

2. Stereochemical models of diphenylethylene and 1,1-diphenylethylene are examined and an explanation is given for the different behavior of these compounds in the polymerization reaction.

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[*] See Consultants Bureau Translation, p. 313.

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MACROMOLECULAR COMPOUNDS.

COMMUNICATION 58. STERIC HINDRANCE IN THE POLYMERIZATION OF NUCLEAR-SUBSTITUTED STYRENES

V. V. Korshak and N. G. Matveeva

In a previous paper we considered the question of the influence of stereochemical factors on the capacity for polymerization of a number of unsymmetrical disubstituted ethylenes and we found the reasons why diphenylethylene gives only a dimer while diphenylenethylene polymerizes very easily [1]. The study of steric hindrance produced by substitution in the styrene nucleus was also of interest and is considered in the present paper.

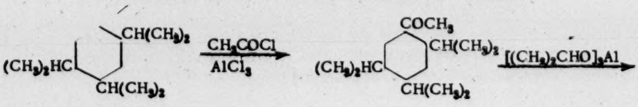
The first systematic study of the polymerization capacities of substituted styrenes was carried out by Shorygin and Shorygina [2]. They studied the polymerization of o-, m- and p-methylstyrenes, o- and p-aminostyrenes, o- and p-methoxystyrenes, o- and p-bromostyrenes, as well as other styrenes, and they established that these styrenes easily polymerize when they are heated to 170-175° for three hours or to 100° for 150 hours.

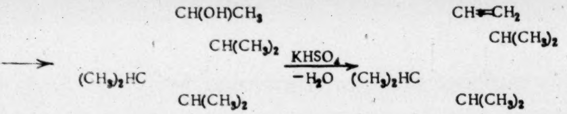
Later, a large number of nuclear-substituted styrenes were obtained and it was shown that the introduction of substituents of a given size into the meta or para position does not bring about hindrance to polymerization. Thus, the polymerization was described of meta- and para-butyl styrenes [3] and m- and p- cyclohexyl styrenes [3] chlorostyrenes [4] p-cyanostyrenes [5] m- and p-iodostyrenes [6], p-carboxystyrenes [7] as well as others [8]. The presence of one substituent in the ortho position does not bring about hindrance to the polymerization process, even when one or two other substituents are present in m- or p-positions of the styrene nucleus. Thus, various di- and tri-substituted styrenes were capable of undergoing polymerization; these had substitutents in the 2,3-, the 2,4-, the 2,5-, the 3,4, the 3,5, the 2,4,5- and the 3,4,5-positions. All the dichloro-substituted styrenes easily polymerized when they were irradiated with ultra violet light [9]. 2,3-, 2,4-, 2,5- and 3,4 dimethylstyrenes also polymerized under the influence of ultra violet radiation [10]. 4-chloro-3-fluoromethylstyrene, 4-chloro-2-trifluoromethylstyrenes, 2,5-, 3,5- and 3,4-di(trifluoromethyl)styrenes, 4-chloro-2,5-di(trifluoromethyl)styrene and 4-chloro-3,5-di(trifluoromethyl) styrene easily polymerized in the presence of perioxide [11] and 5-isopropyl-4-methoxy-2-methyl styrene polymerized under the influence of ultraviolet light [12].

Steric hindrance to polymerization arises only with two substituents in the ortho position, as we observed in 2,6-dimethyl-4-tertiarybutylstyrene, which almost completely lost its capacity for radical polymerization, while, however, retaining its capacity for ionic polymerization [13]. 2,4,6-trimethylstyrene also gives a low-molecular-weight polymer when it is heated for several days at a temperature of 200° [14]. In the case of ortho substituents of large size, as for example, 2,4,6-tri(trifluoromethyl)styrene [15] and 2,4,6-trinitrostyrene [16], the styrenes are completely incapable of undergoing polymerization. Although in the latter case the cause of failure to polymerize is not clear, it is possible that it is not entirely due to steric hindrance, since m-nitrostyrene also failed to polymerize [17], evidently because of the inhibiting action characteristic of nitro compounds. Finally, it should be mentioned that 2,6-dichlorostyrene polymerizes easily on irradiation with ultraviolet light [18].

Thus, the literature indicates that substituents in the m- and p-position do not produce steric hindrance, while the presence of two substituents in the ortho position in some cases hinders the polymerization of di-substituted styrenes. One substituent in the ortho position does not as a rule interfere with polymerization.

Our aim was to find the reason for, and study the nature of the action of ortho substituents in the styrene molecule and for this purpose we synthesized 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene. 2,4,5-triisopropylstyrene was obtained from 1,2,4-triisopropylbenzene which was converted to 2,4,5-triisopropylacetophenone by the action of acetyl chloride in the presence of aluminum chloride. The 2,4,5-triisopropylacetophenone obtained in this way was reduced with aluminum isopropoxide to 2,4,5-triisopropylphenylmethylcarbinol and this was converted to 2,4,5-triisopropylstyrene by heating with potassium bisulfate:




CH(OH)CH$_3$
CH(CH$_3$)$_2$
(CH$_3$)$_2$HC
CH(CH$_3$)$_2$
KHSO$_4$
−H$_2$O
CH=CH$_2$
CH(CH$_3$)$_2$
(CH$_3$)$_2$HC
CH(CH$_3$)$_2$

2,4,5-triisopropylstyrene was found to be a substance very liable to polymerize and was easily converted to a polymer by heating for four hours to 100°, or even on standing at room temperature for two months. After reprecipitation the polymer was obtained in the form of a white powder which softened at 180-195°; the polymer obtained at 100° had a molecular weight of 10,800 and the one obtained at room temperature, a molecular weight of 22,700. •

Thus, it may be concluded that the presence of such a large substituent in the styrene nucleus as the isopropyl group does not hinder polymerization. In Fig. 1, a stereochemical model of 2,4,5-triisopropylstyrene is shown.

From this figure it is evident that the free rotation of the vinyl group is somewhat limited by the presence of the isopropyl group in the ortho position, but all the same the vinyl group is completely accessible for contact with the vinyl group of another monomer molecule which is necessary for successful polymerization.

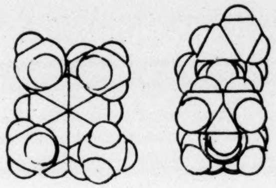
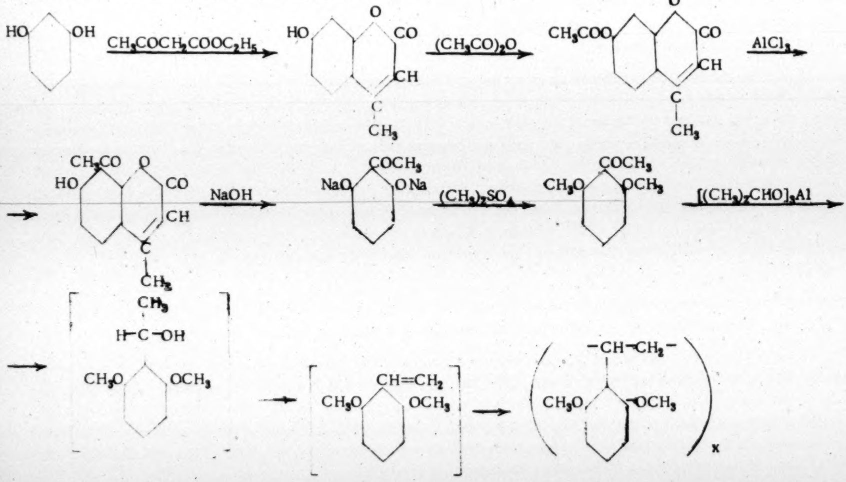


Fig. 1. Stereochemical model of 1,4,5-triisopropylstyrene.

2,6-dimethoxystyrene was obtained as a result of a long series of conversions from 7-hydroxy-4-methylcoumarin. The latter was obtained from resorcinol and acetoacetic ester in the presence of concentrated sulfuric acid. Acetylation of 7-hydroxy-4-methylcoumarin to 7-acetoxy-4-methylcoumarin,(Fries rearrangement of the acetoxy derivatives) and hydrolysis of the rearrangement product afforded 2-acetylresorcinol. Methylation of 2-acetylresorcinol by dimethylsulfate, reduction of 2-methoxyacetophenone by aluminum isopropoxide and dehydration of the carbinol formed resulted in the formation of 2,6-dimethoxystyrene which polymerized at once. The reaction scheme for the preparation of 2,6-dimethoxystyrene is shown below:


HO
OH
CH$_3$COCH$_2$COOC$_2$H$_5$
HO
O
CO
CH
C
CH$_3$
(CH$_3$CO)$_2$O
CH$_3$COO
O
CO
CH
C
CH$_3$
AlCl$_3$
CH$_3$CO
O
HO
CO
CH
C
CH$_3$
NaOH
COCH$_3$
NaO
ONa
(CH$_3$)$_2$SO$_4$
COCH$_3$
CH$_3$O
OCH$_3$
[(CH$_3$)$_2$CHO]$_3$Al
CH$_3$
H−C−OH
CH$_3$O
OCH$_3$
CH=CH$_2$
CH$_3$O
OCH$_3$
−CH−CH$_2$−
CH$_3$O
OCH$_3$
x

• The structure of 2,4,5-triisopropylstyrene which we synthesized was not confirmed experimentally, but it appears to be the most probable structure because the cases described in the literature of the introduction of the acetyl group into 1,2,4-trialkylbenzenes gave 2,4,5-trialkylacetophenones [25].

Poly-2,6-dimethoxystyrene consisted of a thick glasslike resin softening at 78 - 82° with a molecular weight of 3,000. In no experiment did we succeed in obtaining 2,6-dimethoxystyrene in the monomeric form, although we several times reduced with metallic sodium in ethanol and we attempted to follow exactly the conditions of this styrene synthesis described by Shamshurin [19]. This at-first-sight-unexpected tendency of 2,6-dimethoxystyrene to polymerize notably distinguishes it from 2,6-dimethyl-4-tertiarybutylstyrene, which we investigated previously, although the size of the methoxy group should be larger than the methyl, and it would be expected that 2,6-dimethoxystyrene would also lose its ability to undergo radical polymerization. The cause of this difference can only be found by examining the stereochemical models of the molecules of 2,6-dimethoxystyrene and 2,6-dimethyl-4-tertiarybutylstyrene which are shown in figures 2 and 3.

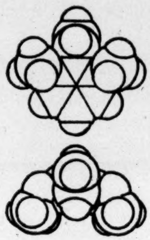


Fig. 2. Stereochemical model of the 2,6-dimethoxystyrene molecule.

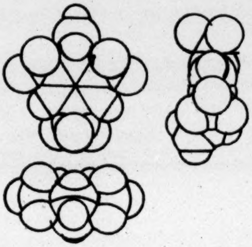
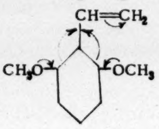


Fig. 3. Stereochemical model of the 2,6-dimethyl-4-tertiarybutylstyrene molecule.

As will be seen from these figures there is a great difference between these compounds. In the case of 2,6-dimethoxystyrene, the methoxy groups in the ortho position are capable of rotating and are so disposed as to allow completely unhindered rotation of the vinyl groups and do not screen them. That is, they do not bring about steric hindrance to polymerization. The oxygen atom, too, which is placed close to the vinyl group, is only slightly larger than the hydrogen atom (radius of the first is equal to 1.4 and of the second 1.2 A) and smaller than the chlorine atom (radius 1.7 A) and still smaller than the methyl group (radius greater than 1.7 A). Therefore, the atom of oxygen itself also does not hinder rotation of the vinyl group and brings about neither a screening nor a blocking effect. On the other hand, the presence of a methoxyl group as has been previously observed by one of us in collaboration with Kolesnikov et al [20] in 2-methoxy-1-vinylnaphthalene leads to the polymerization of the vinyl group and two oxygen atoms must still strongly polarize the double bond of the vinyl group and in this way increase its activity, as is shown in the following diagram.



On examining the arrangement of the 2,6-dimethyl-4-tertiary-butylstyrene we see a different picture. Two methyl groups in the ortho position hold the vinyl group as if in a pincers and do not allow it to come in contact with carbon atoms of another molecule, which is necessary if the polymerization process is to take place. We propose to call this effect "the blocking effect" to distinguish it from the screening effect caused by substituents attached directly to the carbon atoms of the vinyl group [21]. Naturally, the influence of the vinyl effect is greater the greater the size of the ortho substituents. For this reason it is easily seen why 2,6-dichlorostyrene can polymerize and why 2,4,6-tri(trifluoromethyl)styrene cannot, since the size of the trifluoromethyl group is much larger than the chlorine atoms of the methyl group, as can easily be seen in Figs. 3, 4, and 5.

EXPERIMENTAL

2,4,5-Triisopropylacetophenone

To a mixture of 30 g of 1,2,4-triisopropylbenzene, 15 g acetyl chloride and 100 ml tetrachloroethane,

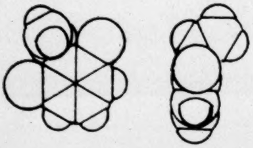


Fig. 4. Stereochemical model of the 2,6-dichlorostyrene molecule

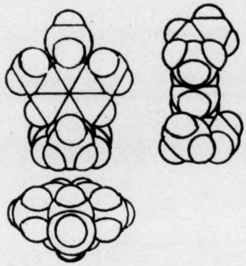


Fig. 5. Stereochemical model of the 2,4,6-tri(fluoromethyl)styrene molecule.

there was added, with cooling, 25 g of aluminum chloride in small portions. The mixture was allowed to stand overnight and then it was heated on a water-bath for an hour, after which it was decomposed by pouring into dilute hydrochloric acid. The organic layer was separated in a separator, washed several times with water and dried over sodium sulfate. The tetrachloroethane was distilled off and the residue distilled under reduced pressure. The fraction boiling between 156 - 162° at 25 mm was collected and recrystallized from ethanol. Yield 22.5 g, i.e. 62.1% of theory. 2,4,5-triisopropylacetophenone consists of long white needles with a sharp incense-like smell, melting at 106 - 107°.

Found %: C 82.78; 82.60; H 10.76; 10.63

$C_{17}H_{26}O$. Calculated %: C 82.86; H 10.64

2,4,5-Triisopropylphenylmethylcarbinol

In a half-liter round-bottomed flask equipped with a reflux condenser were placed 200 ml of absolute isopropanol, 2.5 g of amalgamated aluminum and 0.5 g of mercuric chloride. The flask was then heated to boiling on a water-bath and 2 ml of carbon tetrachloride was added. Almost at once a vigorous reaction commenced and the flask was cooled by means of cold water until the reaction subsided. After this the reaction proceeded to conclusion almost without heating, only at the end was heating on the boiling water bath required to dissolve the aluminum completely.

To the hot solution of aluminum isopropoxide in isopropanol, 10 g of 2,4,5-triisopropylacetophenone was addedand the mixture boiled for three hours. The reflux condenser was then changed for a straight condenser, the isopropanol and acetone distilled off, the residual mass was poured into water acidified with hydrochloric acid and 50 ml of benzene was added. The benzene solution was separated, washed with water and dried over sodium sulfate. The benzene was then distilled off. 2,4,5-triisopropylphenylmethylcarbinol was distilled under reduced pressure and the fraction coming over between 126 and 127° at 3 mm was collected. The yield was 58.03% of the theoretical. 2,4,5-triisopropylphenylmethylcarbinol after recrystallization from ether was obtained in the form of white needles melting at 93 - 94°.

Found %: C 81.90; 81.69; H 11.30; 11.38

$C_{17}H_{18}O$. Calculated %: C 82.29; H 11.36

Phenylurethane of 2,4,5-triisopropylphenylmethylcarbinol

To 2 g of 2,4,5-triisopropylphenylmethylcarbinol dissolved in 20 ml of absolute benzene, 1 g of phenylisocyanate was added and the mixture was boiled half an hour. The benzene was then distilled off and the phenylurethane recrystallized from alcohol. Yield 2.47 g or 82.6% of theory. Phenylurethane of 2,4,5-triisopropylphenylmethylcarbinol consisted of small white needles melting at 180 - 180.5°.

Found %: C 78.17; 78.35; H 9.10; 8.92; N 3.96; 3.87

$C_{24}H_{33}O_2N$. Calculated %: C 78.47; H 8.99 N 3.81

2,4,5-Triisopropylstyrene

In a Claisen flask 13 g of 2,4,5-triisopropylphenylmethylcarbinol and 2 g of potassium bisulfate were placed and the mixture distilled under reduced pressure so that styrene was distilled off at a temperature of 160 - 200°. The styrene collected was dried over sodium sulfate and redistilled once again under reduced pressure.

2,4,5-triisopropylstyrene boils at 165-166° at 75 mm. Yield 7.6 g, i.e. 63.12% of theory. d_4^{20} 0.9018; n_D^{20} 1.5075, MR_D 75.09. Calculated MR_D 76.89.

Found %: C 88.28; 88.41; H 11.18; 11.31
$C_{17}H_{26}$. Calculated %: C 88.62; H 11.36.

Polymerization of 2,4,5-triisopropylstyrene

1 g of 2,4,5-triisopropylstyrene was placed in an ampoule and the air was removed by repeated flushing with nitrogen. The sealed ampoule was placed in a boiling water bath and heated for four hours. The ampoule was then opened and the polymer reprecipitated by pouring a benzene solution into methanol followed by drying. The molecular weight by the viscosity method was found to be 10,800. Another sample of the styrene was allowed to stand at room temperature for two months. The molecular weight of this polymer was 22,700.

Found %: C 88.16; 88.50; H 11.12; 11.28
$C_{17}H_{26}$. Calculated %: C 88.62; H 11.36

7-Hydroxy-4-methylcoumarin

To 450 g of sulfuric acid (sp.gr. 1.84) cooled by a freezing mixture, there was added with stirring a mixture of 110 g of resorcinol and 130 g of aceto-acetic ester, at such a rate that the temperature of the reaction mixture did not exceed 0°. After the addition had been completed the mixture was allowed to stand at 0° for four hours with occasional stirring and it was then poured dropwise with vigorous stirring on to a mixture of ice and water. The bright yellow precipitate formed was removed by filtration and thoroughly washed with water and dried in air. The air-dried product was dissolved in dilute alkali and precipitated with hydrochloric acid [22]. Yield 162.3 g, that is 92.21% of theory. 7-hydroxy-4-methylcoumarin after recrystallization from ethanol consisted of a bright yellow powder melting at 188-188.5°.

Found %: C 68.07; 67.86; H 4.31; 4.48
$C_{10}H_8O_3$. Calculated %: C 68.17; H 4.57

7-Acetoxy-4-methylcoumarin

To a mixture of 30 g of alkali 100 ml of water and 500 g of ice, 88 g of 7-hydroxy-4-methylcoumarin was added. To the coumarin solution, still containing a certain amount of ice 60 g of acetic anhydride was added. The flask was closed with a stopper and vigorously shaken. The acetate, precipitated as a white mass, was filtered off, washed several times with water and dried in air [22]. Yield 96.3 g or 95.73% of theory. 7-acetoxy-4-methylcoumarin after recrystallization from ethanol was obtained as long, fine needles melting at 153-154°.

Found %: C 65.76; 65.42; H 5.02; 4.77
$C_{12}H_{10}O_3$. Calculated %: C 66.04 H 4.62

7-Hydroxy-8-acetyl-4-methylcoumarin

A mixture of 50 g of 7-acetoxy-4-methylcoumarin and 125 g of aluminum chloride was placed in a round-bottomed flask fitted with an air condenser and this was heated on a glycerol bath to 160° for three hours [24]. The reaction mixture was then decomposed by pouring it into ice-cooled dilute hydrochloric acid. The bright grey product formed was filtered off and washed several times with water. The product was then dissolved in a small quantity of 10% sodium carbonate solution. The insoluble part was removed by filtration and 7-hydroxy-8-acetyl-4-methylcoumarin was precipitated from the filtrate by the addition of hydrochloric acid. The precipitate was filtered off, washed with water and dried. Yield 11.2 g or 37.3% of theory. 7-hydroxy-8-acetyl-4-methylcoumarin after recrystallization from aqueous ethanol was obtained as small leaves of sandlike color melting at 167-168°.

Found %: C 65.47; 65.70; H 4.66; 4.73
$C_{10}H_8O_3$. Calculated %: C 66.04 H 4.62

Acetyl Resorcinol

In a 2-necked flask equipped with a reflux condenser, 26 g of 7-hydroxy-4-methylcoumarin and 240 mls of 12% solution of sodium hydroxide were placed and nitrogen was passed in through a tube not reaching quite to the surface; the flask was then heated on a boiling water bath for 6 hours [19]. The reaction mixture was then cooled and the acetyl resorcinol precipitated with hydrochloric acid and recrystallized from water. Yield 12.4 g or 68.1% of theory. Acetyl resorcinol on recrystallizing twice from water was obtained as a bright yellow powder melting at 155-156°.

Found %: C 62.74; 62.82; H 5.39; 5.18
$C_8H_8O_3$. Calculated %: C 63.14; H 5.30

2,6-Dimethoxyacetophenone

In a 2-necked flask fitted with a reflux condenser and a dropping funnel, 12 g of acetyl resorcinol and 120 ml of 12% solution of sodium hydroxide were placed [19]. The reaction mixture was heated to boiling, the heating was then stopped and 100 g of dimethyl sulfate was added in small portions. When about 2/3rds of the dimethyl sulfate had been added, 60 ml of 12% solution of sodium hydroxide was added followed by the remainder of the dimethyl sulfate. Care was taken to keep the medium alkaline. The reaction mixture was then boiled for half an hour and after cooling the 2,6-dimethoxy acetophenone formed was filtered off, washed with water and recrystallized from water. Yield 10.2 g or 70.8% of theory. 2,6-dimethoxyacetophenone was a bright yellow substance melting at 69-70°. Shamshurin [19] gives a melting point of 72-73°.

Found %: C 66.34; 66.46; H 6.63; 6.84
$C_{10}H_{12}O_3$. Calculated %: C 66.66; H 6.71

2,6-Dimethoxystyrene polymer

Aluminum isopropoxide was prepared from 2.5 g of amalgamated aluminum and 100 ml of absolute isopropanol in a round-bottomed flask fitted with a reflux condenser as previously described. To the aluminum isopropoxide obtained, 10 g of dimethoxyacetophenone was added and the reaction mixture was boiled for 2½ hours, after which the reflux condenser was changed and the isopropanol and acetone were distilled off. When the isopropanol had been removed the residual mass was poured into water acidified with hydrochloric acid.

The aqueous layer was extracted with benzene. The benzene layer was washed several times with water and then dried over anhydrous sodium sulfate. The benzene was removed by distillation and a solid residue of polymer having a dark brown color and melting at 78-82° was obtained. Yield 5.8 g or 63.3% of theory. The molecular weight of poly-2,6-dimethoxystyrene determined by the viscosity method in benzene solution was found to be 3060. Attempts to prepare the monomer by depolymerization of the polymer were not successful since the monomer formed immediately polymerized on the walls of the flask as a solid layer.

Found %: C 72.88; 72.74; H 7.39; 7.36.
$C_{10}H_{12}O_2$. Calculated %: C 73.13; H 7.37.

The reduction of 2,6-dimethoxyacetophenone was also carried out with metallic sodium in ethanol by the method described by Shamshurin [19] but in this case also no monomeric 2-methoxystyrene was obtained.

SUMMARY

1. It is shown that the isopropyl group in the ortho position of the styrene molecule does not cause steric hindrance in the polymerization process.

2. It is shown that 2-methoxyl groups in the ortho position of the styrene molecule do not hinder polymerization.

3. 2,4,5-triisopropylacetophenone and 2,4,5-triisopropylstyrene have been synthesized.

4. Polymers of 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene have been prepared.

5. An explanation based on stereochemical grounds is given for the absence of steric hindrance in the polymerization of 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene; an explanation is also given for the occurrence of steric hindrance in the polymerization of 2,6-dimethyl-4-tertiarybutylstyrene and 2,4,6-tri-(fluoromethyl)styrene.

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THE INDIRECT VINYLATION OF MONOCARBOXYLIC AND HYDROXY ACIDS

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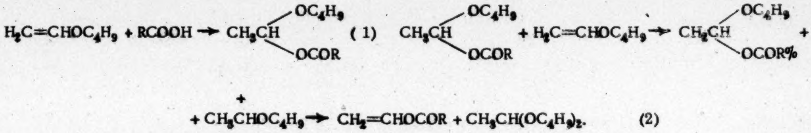
The synthesis of vinyl esters of organic acids and acetylene is familiar not only in the laboratory but also in industry [1]. The use of vinyl acetate for the transesterification of the corresponding acids [2] is a new application in the preparation of similar substances. We have attempted to replace the vinyl acetate by more readily accessible compounds—the vinyl ethers. It should be mentioned that the interaction of vinyl ethers and monocarboxylic acids has only been studied for incomplete acylals. This reaction proceeds when the starting components are taken in molecular proportions and heated. If an excess of vinyl butyl ether and an acid catalyst is used, then the main product obtained is a vinyl ester.

The mechanism of the formation of vinyl esters from acids and vinyl ethers is shown in the following scheme. At first an incomplete acylal (1) is formed. With excess of vinyl butyl ether the acylal is converted to an ion and then to an ester (2).



$$H_2C{=}CHOC_4H_9 + RCOOH \rightarrow CH_3CH\begin{matrix}OC_4H_9\\OCOR\end{matrix} \quad (1) \qquad CH_3CH\begin{matrix}OC_4H_9\\OCOR\end{matrix} + H_2C{=}CHOC_4H_9 \rightarrow CH_2CH\begin{matrix}OC_4H_9\\OCOR\%\end{matrix} +$$

$$+\,CH_3\overset{+}{C}HOC_4H_9 \rightarrow CH_2{=}CHOCOR + CH_3CH(OC_4H_9)_2. \qquad (2)$$

In this way, evidently, conditions are created which promote the fission of the elements of butyl alcohol and the transfer of the acylal to a vinyl ester.

The vinyl butyl ether transesterification reaction brought about by monocarboxylic acid and hydroxy acids proceeds most successfully when the proportions are 1 molecule of acid to 5 molecules of ether. This process, because of its simplicity, is more suitable and accessible than the direct vinylation of acids. Experiments have shown that phosphoric anhydride is a specific catalyst; this is used together with phosphoric acid also in the direct vinylation of carboxylic acids [4]. With this catalyst the yield of vinyl esters is twice as great as that obtained with hydrochloric or sulfuric acid. The transesterification of vinyl butyl ether by means of organic acids has been most extensively studied in the case of caproic acid. The good results obtained have been extended to other acids.

From Table 1 it follows that caproic acid and vinyl butyl ether are best used in the proportion of 1:5; these give the highest yield of vinyl ester.

TABLE 1
Transesterification of Vinyl Butyl Ether by Caproic Acid in the Presence of Phosphoric Anhydride

Reaction temperature in °C	Proportion of acid and ether	Yield of vinyl ester expressed as % of acid
160-165	1:1	Traces
160-165	1:2	4
160-165	1:3	19
160-165	1:4	34
160-165	1:5	47

TABLE 2
Transesterification of Vinyl Butyl Ether by Organic Acids in the Presence of Different Catalysts.

Acid	Reaction temperature, °C	Yield of vinyl ester calculated on acid % with catalyst.		
		HCl	H_2SO_4	P_2O_5
Acetic	115-120	none	none	1
Proprionic	130-140	"	"	2
Butyric	140-150	19	20	45
Valeric	150-160	18	19	47
Caproic	160-165	17	20	47
Lactic	90-100	7	7	15
β-Hydroxybutyric	120-135	8	9	18

The transesterification of vinyl butyl ether by caproic acid proceeds with a spontaneous rise in temperature up to 160 - 165°. The reaction continues for one hour, including the time required for the temperature to drop to the initial. With a 5-fold excess of vinylbutyl ether over the quantity of acid taken, as well as vinyl caproate $H_2C{=}CHOC_5H_{11}$ there are formed butoxyethylidine caproate $CH_3CH(OC_4H_9)OCOC_5H_{11}$, dibutyl acetal $CH_3CH(OC_4H_9)_2$, butyl caproate $C_4H_9OCOC_5H_{11}$, and also traces of butyl alcohol C_4H_9OH and acetaldehyde CH_3CHO. When caproic acid reacts with 1 - 4 equivalents of ether, the same products are formed but the quantity of vinyl caproate (Table 1) is less and the yield of incomplete acylals increases. The use of 6 - 7 equivalents of ether in the reaction mixture does not affect the yield of vinyl caproate.

The transesterification of vinylbutyl ether by monocarboxylic acids C_2 to C_5 (Table 2) showed that this process is similar to the one described for caproic acid The rise in temperature due to the exothermic reaction effect reaches a value close to the boiling temperature of the starting acids. Under these conditions vinyl acetate and vinyl propionate were obtained in small quantities (1 -2%). An attempt to increase the yield of these esters by raising the temperature to 160 - 170° (autoclave) gave negative results. It is also of interest to note that the formation of vinyl lactate and vinyl hydroxybutyrate takes place at a temperature considerably below the boiling point of lactic (122°/15 mm) and hydroxybutyric (130°/12 mm) acids. Of the three catalysts tried the best was found to be phosphoric anhydride.

TABLE 3

Characteristics of Vinyl Esters of Monocarboxylic Acids and Hydroxy Acids

Name and formula of ester	B.p. °C	d_4^{20}	n_D^{20}	MR_D Found / Calculated
Vinyl butyrate $C_3H_7COOCH{=}CH_2$	112 - 113.0	0.9121	1.4057	30.745 31.205
Vinyl valerianate $C_4H_9COOCH{=}CH_2$	184 - 136.0	0.9070	1.4102	35.025 35.843
Vinyl caproate $C_5H_{11}COOCH{=}CH_2$	168 - 170.0	0.8965	1.4160	39.824 40.481
Vinyl lactate $CH_3CHOHCOOCH{=}CH_2$ *	151 - 153.0	1.0604	1.4088	27.060 28.092
Vinyl β-hydroxybutyrate $CH_3CHOHCH_2COOCH{=}CH_2$	170 - 173.0	1.0713	1.4136	31.819 32.730

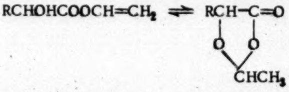
* Reported for the first time.

Note: 1) All the vinyl esters went yellow on standing.

2) The vinyl esters of the hydroxy acids were hydrolyzed by atmospheric moisture.

From Table 3 it will be seen that the boiling point of the esters increases with temperature, while the density decreases. The change in the color of the esters on storage is due to their slow oxidation by atmospheric oxygen in the presence of light. If the esters are stored in the dark or in colored bottles they undergo practically no change.

The vinyl esters of lactic and hydroxybutyric acids readily absorb moisture and hydrolyze with the separation of acetaldehyde and the corresponding acid and for this reason they must be distilled in a stream of dry nitrogen. These compounds boil within a range of 2 to 3° and their molecular refractions are lower than the calculated values. It is possible that these anomalies are due to the presence in the ethers of both a linear and a cyclic form in equilibrium.



An indirect indication of tautomery is seen in the molecular refraction values. Thus, for example, for vinyl acetate the calculated MR is 28.092, the cyclic form corresponding only to 26.359. The value found for MR is 27.060. Vinyl acetate and vinyl β-hydroxybutyrate are soluble in ethyl ether, ethanol, acetone and benzene. They are hydrolyzed to the corresponding acids and acetaldehyde, by aqueous solutions of alkalies and by mineral acids.

EXPERIMENTAL

Transesterification of vinyl butyl ester of caproic acid in the presence of phosphoric anhydride.

Starting materials: caproic acid with boiling point 202 - 203°; d_4^{20}, 0.9290, n_D^{20} 1.4145; vinyl butyl ether with boiling point 93.5 - 94°; d_4^{20} 0.7790; n_D^{20} 1.4025, and phosphoric anhydride — air dry.

Into a round-bottomed 3-necked flask are placed 23.2 g (10.2 moles) of caproic acid, 100 g(1 mole) of vinylbutyl ether and about 0.1 g of phosphoric acid; the flask is fitted with a mechanical stirrer, a mercury seal, a large capacity reflux condenser connected to a bulb trap, and a thermometer reaching to the bottom of the flask. On mixing, the temperature of the reaction mixture rose and after 15 or 20 minutes after the commencement of the experiment the temperature reached 80-85°. The flask was cooled with ice-water, the temperature rising to 160-165°. The mixture was then cooled to room temperature over 35-40 minutes. After the reaction had concluded traces of acetaldehyde (characteristic odor) were observed in the trap.

After the brown mixture had been neutralized with potash and the residue filtered off, 72.5 g (75% of amount taken) of vinylbutyl ether was distilled off at 93-98°. The vinylbutyl ether was treated with metallic sodium and had the following constants after distillation: boiling point 93.5-94.0°; n_D^{20} 1.4025. The constants of the ether separated agreed with those of that taken in the reaction. The residual mixture was distilled under reduced pressure in a stream of dry nitrogen and the following fractions were obtained:

Fraction 1 boiling point 30-40°/3 mm; 15.2 g; n_D^{20} 1.4150
Fraction 2 boiling point 42-46°/3 mm; 3.6 g; n_D^{20} 1.4083
Fraction 3 boiling point 57-63°/3 mm; 2.3 g; n_D^{20} 1.4108
Fraction 4 boiling point 85-90°/3 mm; 16.2 g; n_D^{20} 1.4128
Fraction 5 resinous residue in the flask 5.3 g; not further investigated.

Loss 6.6 g; collected in trap 1.5 g; n_D^{20} 1.4140.

Repeated distillation of fraction 1, combined with the contents of the trap under normal pressure gave a substance with the following characteristics: b.p. 168-170°; d_4^{20} 0.8995; n_D^{20} 1.4160, which corresponds to vinyl caproate. Literature data: b.p. 169-170°; n_D^{20} 1.4160 [5]. Yield 13.35 g (47%).

Hydrolysis of vinyl caproate by ethanolic potassium hydroxide
Found %: $C_5H_{11}COOCH{=}CH_2$ 98.3 and 101.52.

On hydrolysis, acetaldehyde separated as found by its characteristic odor. Vinyl caproate decolorized bromine water and added hydrogen. In the latter case it was hydrolyzed to ethyl caproate.

Hydrogenation of Vinyl Caproate

20 g of freshly distilled vinyl caproate (0.2 mole) and 5.8 g of Raney nickel catalyst (20% by weight of starting ester) were placed in a half-liter autoclave. Hydrogen was admitted and an initial pressure of 90-130 atm. was established in the autoclave. It was then rotated. After an hour the temperature had increased to 32°, and the hydrogen added vigorously. The hydrogenation was completed in 2-3 hours. After room temperature and constant pressure had been established in the autoclave, the mixture was withdrawn and distilled in a Favorsky flask under normal pressure. Double distillation gave chemically pure ethyl caproate; b.p. 151-152°; d_4^{20} 0.8649; n_D^{20} 1.4046; yield 26.0 g (89% of theory). The literature gives: b.p. 151°; d_4^{20} 0.8648; n_D^{20} 1.4045 [5].

Fraction II was treated with metallic sodium. The precipitate was filtered off and the filtrate redistilled. A pure substance (2.1 g) with b.p. 184-185°; n_D^{20} 1.4090 was obtained. The data points to its identity with dibutylacetal.

Fraction III, after redistillation had the constants; b.p. 61-62°/3mm; n_D^{20} 1.4110; d_4^{20} 0.8636. Yield 1.7 g (0.5%). These constants correspond to butyl caproate $C_5H_{11}COOC_4H_9$.

Hydrolysis of butyl caproate by ethanolic potassium hydroxide
Found %: $C_5H_{11}COOC_4H_9$ 99.12 and 98.96.

Fraction IV was redistilled in a current of dry nitrogen under reduced pressure A yield of 13.33 g (28%) of butoxyethylidene caproate was obtained; b.p. 88-90.0°/3 mm; n_D^{20} 1.4140.

Hydrolysis and determination of butyoxyethylidene caproate through the acid
Found %: $CH_3CH(OC_4H_9)OCOC_5H_{11}$ 99.4 and 101.2

Transesterification of the Vinylbutyl Ester of Lactic Acid

Starting materials: lactic acid with b.p. 122°/15 mm; d_4^{20} 1.2400; 18 g (0.2 mole); vinylbutyl ether with b.p. 93.5-94°; d_4^{20} 0.7790; n_D^{20} 1.4022; 100 g (1 mole); phosphoric anhydride—air-dry 0.1 g.

The experiment was carried out in the same way as the previous one. After the catalyst had been introduced, the maximum temperature reached by the mixture was 90-100°. The mixture darkened and resinified. After treatment with potash the filtrate was fractionated in a current of dry nitrogen; the following fractions were obtained:

Fraction 1 b.p. 92-94°; n_D^{20} 1.4020; 89.4 g
Fraction 2 b.p. 148-153°; n_D^{20} 1.4069; 5.4 g
Fraction 3 b.p. 180-184°; n_D^{20} 1.4092; 4.3 g
Fraction 4 b.p. 188-189°; n_D^{20} 1.4196; 5.6 g
Loss(by difference) 13.3 g

Fraction I, after treatment with sodium, redistilled at 93-94°; n_D^{20} 1.4022; d_4^{20} 0.7790. The constants correspond to vinylbutyl ether. Recovery from the reaction 85.1 g (85.1%).

Fraction II, after a second redistillation showed the following constants: b.p. 151-153°; d_4^{20} 1.064; n_D^{20} 1.4088; yield 3.5 g (15%); Found MR 27.060; calculated for $C_5H_8O_3$ MR_D 28.092.

Found: M 115.19; 114.31 (cryoscopic in benzene solution)
Calculated: M 116,114
Found %: C 51.66; 51.50; H 7.28; 7.08
$C_5H_8O_3$. Calculated %: C 51.72; H 6.94
Hydrolysis and determination of vinyl lactate through acetaldehyde
Found %: 98.4; 95.7
Hydrolysis and determination of vinyl lactate through the acid
Found %: 100.7; 100.1

Fraction III, after treatment with metallic sodium, had the following characteristics: b.p. 184-185°; n_D^{20} 1.4089. The constants correspond to dibutylacetal. Yield 3.4 g.

Hydrolysis and determination of dibutylacetal through acetaldehyde
Found %: 98.6; 100.6.

Fraction IV, after twice redistilling, had b.p. 188-189°; n_D^{20} 1.4195; d_4^{20} 0.9683; yield 5.2 g (13.4%). This material corresponds to butoxyethylidene lactate [6] $CH_3CH(OC_4H_9)OCOCHOHCH_3$. Found MR 48,556; calculated for $C_9H_{18}O_4$ MR 48 585.

Found: M 185.21; 193.83 (cryoscopic in benzene solution).
Calculated: M 190.234
Found %: C 57.10; 56.88; H 9.65; 9.64
$C_9H_{18}O_4$. Calculated %: C 56.84; H 9.47
Hydrolysis and determination of acylal through acetaldehyde
Found %: 96.8; 96.2

Transesterification of Vinylbutyl Ester of β-Hydroxybutyric Acid

Starting materials: β-Hydroxybutyric Acid, m.p. 49°, b.p. 130°/12 mm, 10.4 g (0.1 mole); vinylbutyl ether, b.p. 93-94°; n_D^{20} 1.4024, 50 g (0.5 mole); phosphoric anhydride 0.05 g.

The synthesis and separation of the products were carried out as in the previous experiment. The temperature of the reaction mixture rose spontaneously to 135°. Redistillation separated: 43 g (86%) of vinylbutyl ether; 2.35 g (18% as shown by the acid) of vinyl-β-hydroxybutyrate and 3.8 g of dibutylacetal. Vinyl-β-hydroxy butyrate $CH_3CHOHCH_2COOCH{=}CH_2$ had b.p. 170-173°; d_4^{20} 1.0713. n_D^{20} 1.4136; found MR 31,819; calculated for $C_6H_{10}O_3$ MR 32,750.

Found M 129.4; 124.1 (cryoscopic in benzene solution).
$C_6H_{10}O_3$. Calculated: M 130.24.
Found %: C 55.57; 55.78; H 7.69; 7.72
$C_6H_{10}O_3$. Calculated %: C 55.35; H 7.69
Hydrolysis and determination of vinyl-β-hydroxybutyrate through the acetaldehyde.
Found %: 96.8, 95.3.
Hydrolysis and determination of vinyl-β-hydroxybutyrate through the acid
Found %: 100.1; 100.6

Dibutylacetal $CH_3CH(OC_4H_9)_2$ had b.p. 185°, n_D^{19} 1.4090.

Hydrolysis and determination of dibutylacetal through acetaldehyde
Found %: 95.2; 96.2

SUMMARY

1. A new method is proposed for the indirect vinylation of monocarboxylic and hydroxyacids by transesterification of the corresponding acid with the readily available vinylbutyl ether in the presence of phosphoric anhydride.

2. The vinyl esters are obtained in 47% yield.

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THE CHLORINATION OF HYDROLYSIS LIGNIN

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Hydrolysis lignin, which is obtained in large quantities as a by-product of the hydrolysis industry, is a high-molecular-weight compound whose structural elements consist of phenols, and it is therefore a potentially valuable material which might find uses in different branches of the national economy. However, hydrolysis lignin is infusible, insoluble, chemically of low activity and it cannot be decomposed into valuable low-molecular-weight compounds by simple methods. It seemed to us that the chlorination of lignin is one of the methods by which it could be converted to a reactive state. Lignin occurring in the walls of plant cellulose and isolated from plants is easily chlorinated by treating these materials with chlorine. The properties of the chlorolignin obtained are determined by the nature of the starting materials, the chlorine content and the chlorination conditions. The chlorination is accompanied by the evolution of hydrogen chloride.

There is disagreement as to the nature of the interaction of chlorine with lignin. Some workers, studying the halogenation of lignin, consider that chlorine and bromine react with lignin only by substitution [1, 2, 3], while others consider that, as well as substitutions, additions also take place [4, 5]. When lignin is chlorinated, a loss of methoxyl groups occurs. Harris, Scherrer and Mitchell [5] found that fir lignin containing 17.3% of OCH_3 had only 6.1% after chlorination. The OCH_3 content of lignin is reduced in a somewhat lesser degree by bromination. Hibbert and his co-workers [4] also observed a reduction in the content of OCH_3 groups on halogenation. According to Harris [6], lignin sulfate from hard wood loses one-third of its methoxyl on chlorination, while for lignin of soft wood the loss is about two-fifths. Harris, Scherrer and Mitchell found that when lignin is chlorinated hydroxyl groups are lost. According to these workers, lignins when they are chlorinated both in CCl_4 and in water are neither methylated nor acetylated. Unfortunately, the halogenation conditions are not given. From these short literature references it will be seen that the chlorination of lignin proceeds in a complicated manner and is accompanied by side reactions.

In chlorinating hydrolysis lignin we avoided an excess of chlorine and high temperatures in order not to destroy the lignin molecule and we carried out chlorination under mild conditions; at low temperatures (20°) and with the required quantity of chlorine in the dark and in both carbon tetrachloride and water without a catalyst. Chlorination at a high temperature with a large excess of chlorine leads to the destruction of the side chains in the lignin molecule [7].

EXPERIMENTAL

Technical hydrolysis lignins from the Leningrad and Archangel hydrolysis factories, the characteristics of which are given in Table 1, were chlorinated:

TABLE 1

Source of lignin	Content of reducing substances in %	Content of lignin %	Resin content %	Acid content, calc'd as H_2SO_4 %
Lignin from the Leningrad factory	2.47	88.23	4.57	1.2
Lignin from the Archangel factory	2.34	93.54	9.26	1.53

Lignin ground in ball mill was extracted with boiling water, air-dried at room temperature and then twice extracted with dichloroethane to remove resins (boiling under reflux for four hours). The lignin was filtered off, washed with dichloroethane, dried in air and then over P_2O_5. 50 g samples of lignin were used for chlorination and this was carried out in dark vessels with ground stoppers, by shaking with chlorine water or chlorine solution in carbon tetrachloride for an hour at 20°.

The chlorine water was prepared by saturating water with chlorine at 12°. The chlorine in carbon tetrachloride was prepared by passing a stream of chlorine into cold carbon tetrachloride. The concentrated solution

TABLE 2

Expt. No.	Quantity of Cl_2 required (%)	Quantity of Cl_2 obtained (%)	Yield of chloro-lignin, as % of initial	OH group content, (%)	OCH_3 group content (%)	Composition of substance calculated on C_9
1	2	3	4	5	6	7
Chlorination in CCl_4						
Lignin of the Leningrad hydrolysis factory						
Starting lignin			–	7.33	9	$C_9H_{10.06}O_{3.35}$
1	5.0	4.77	99.12	8.37	–	–
2	10.0	10.0	91.62	6.53	7.30	$C_9H_{9.45}Cl_{0.57}O_{4.18}$
3	20.0	19.53	95.91	6.56	–	$C_9H_{8.01}Cl_{1.22}O_{3.91}$
4	30.0	27.33	88.50	6.58	3.92	$C_9H_{8.34}Cl_{1.36}O_{3.69}$
Chlorination in CCl_4						
Lignin of the Archangel hydrolysis factory						
Starting lignin			–	9.16	–	–
1	5.0	5.00	–	8.59	–	–
2	10.0	9.89	–	–	–	–
3	20.0	18.39	–	8.04	–	–
4	25.0	22.26	–	7.06	–	–

of Cl_2 in CCl_4 was kept in dark vessels with ground stoppers, but the chlorine water was prepared directly for each experiment and analyzed. The chlorine water and the solution of Cl_2 in CCl_4 were used in quantities calculated for the substitution reaction, that is twice the quantity to be introduced into the lignin. Usually the chlorine water contained 5-6 g Cl_2 per liter and the proportion of chlorine necessary for the reaction was determined. In chlorinating with the carbon tetrachloride solution the proportion used was 1:1.5.

From the Leningrad lignin, samples of chlorolignin containing ~5, 10, 20, and 30% of chlorine were prepared by chlorination both in water and in CCl_4: from the Archangel lignin, samples were prepared containing ~5, 10, 20, and 25% of chlorine. The chlorine was quantitatively removed from the reaction solutions (no reaction with starch iodide paper). In the preparation of highly chlorinated lignins, insignificant traces of chlorine remained in the solutions. The chlorinated samples were thoroughly washed with water until the washings were neutral to methyl orange, then dried at first in air and finally in a vacuum desiccator over P_2O_5. The highly chlorinated products were colored orange-brown. All the samples were analyzed for chlorine, hydroxyl groups, and methoxyl groups.

The hydroxyl groups were determined by Verley's method. Since treatment of the chlorolignins in pyridine resulted in elimination of part of the chlorine as HCl, and since the chlorolignins contain active hydrogen groups titratable by alkali, a blank experiment was carried out in each case: the sample of chlorolignin was heated with pyridine under the Verley conditions. In calculating the percentage of hydroxyl groups, a correction was made for the number of milliliters of alkali used in the blank experiment.

Because several samples of chlorolignin, especially those highly chlorinated, dissolved in pyridine with the formation of dark solutions which were difficult to titrate with phenolphthalein, in all cases we used the titration method in which a drop of the solution was removed on a strip of filter paper previously moistened with thymol-blue indicator solution, which sharply changes at a pH close to that of phenolphthalein. The paper was dried before use. The end of the titration with alkali was determined by the formation of a pale blue streak. The blank titrations were carried out in the same way The methoxyl groups were determined by the Kirpal-Byun method. The results obtained are shown in Table 2.

Average weight of structure link	Content of OH groups in the starting lignin calculated on the structure chain of chlorolignin	Content of OCH_3 groups in the starting lignin calculated on the structure link of the chlorinated lignin	Quantity of chlorine required (%)	Quantity of chlorine obtained (%)	Yield of chlorolignin (% of initial)	Content of OH groups (%)	Content of OCH_3 groups (%)
8	9	10	11	12	13	14	15
Chlorination in H_2O Lignin of the Leningrad hydrolysis factory							
171.7	–	–	–	–	–	7.83	9.00
–	–	–	5.0	6.15	92.09	7.28	–
204.64	6.57	7.55	10.0	12.40	95.97	6.47	4.62
222.03	6.05	6.96	20.0	19.37	100	6.00	–
241.48	5.57	6.36	30.0	24.02	95.81	–	1.33
Chlorination in H_2O Lignin of the Archangel hydrolysis factory							
–	–	–	–	–	–	9.16	–
–	–	–	5.0	7.01	–	8.13	–
–	–	–	10.0	10.52	–	–	–
–	–	–	20.0	20.03	–	8.42	–
–	–	–	25.0	20.65	–	7.26	–

From Table 2 it is evident that on chlorination in carbon tetrachloride the quantity of chlorine introduced into the lignin is close to that taken (5, 10, 20, 30% and 5, 10, 20, 25%). On chlorination with chlorine water, deviations from the amounts taken are observed. For low degrees of chlorination, the Cl content is higher than that taken (I, II) and for high degrees (IV) lower than that required. Only with 20% of chlorine is the quanitity of halogen introduced equivalent to that required. The data are the same for the lignins from the Leningrad and Archangel factories.

Evidently, when lignin is chlorinated in CCl_4 at 20° in the absence of moisture, the reaction is mainly substitution (somewhat lower contents of chlorine compared with the amounts required in the highly chlorinated preparations may be explained by the loss of chlorine when these are treated in fairly concentrated solutions in CCl_4). On chlorination with chlorine water there is a deviation from the main type of reaction.

The percentage OH group content determined with allowance for the acidity of the preparations and for the HCl eliminated is independent, apart from small variations, of the chlorine content in the samples chlorinated both in CCl_4 and in H_2O. If it is reckoned that the molecular weight of the structural elements of chlorinated lignin is higher than the starting, then the theoretically calculated quantity of OH groups in the chlorolignins should be lower than in the starting lignins. In calculating the average weight of the elementary lignin link and the average weights of the elementary links in the chlorolignin molecules, elementary analyses were used.

From columns 5 and 9 in Table 2, it is evident that the content of OH groups in lignin on chlorination closely corresponds with the calculated values, consequently the OH groups of lignin do not appear to take part in the chlorination, or the number of groups disappearing during the process is compensated for by the destruction of the lignin. This does not agree with the results of American investigators, who consider that on halogenation the hydroxyl groups of lignin disappear (it is true in the paper the method of halogentaion is not given). The content of OCH_3 groups in chlorinated lignin decreases as the chlorine increases. A marked decrease is observed when chlorination is in water. This agrees with the results already known in the literature.

SUMMARY

1. Technical hydrolysis lignin is easily chlorinated at 20° by solutions of chlorine in carbon tetrachloride or by chlorine water. When 25-27% of chlorine is introduced, the latter is quantitatively removed from the solution by the lignin.

2. The chlorine content of products chlorinated in carbon tetrachloride is very close to that required by calculation for the substitution reaction.

3. When lignin is chlorinated both in carbon tetrachloride and in water at 20° in the absence of excess chlorine and catalysts, the number of hydroxyl groups in the lignin remains unchanged. These results do not agree with those obtained by American authors who consider that hydroxyl groups are removed from lignin by halogenation.

4. The content of methoxyl groups in lignin is reduced on chlorination even under mild conditions. The reduction is expecially marked when chlorination is carried out by chlorine water.

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OBITUARY

GEORGY VLADIMIROVICH AKIMOV

On January 23, 1953, after a serious illness, there passed away the outstanding physical chemist of our country, the greatest representative of Soviet science in the field of corrosion and metallurgy, Georgy Vladimirovich Akimov.

In the development of the science of corrosion of metals our country has always occupied one of the leading places. The outstanding successes in the science of metal corrosion in the past twenty years are indissolubly connected with the name of the talented Soviet scientist-Communist Honored Worker in Science and Technology, Georgy Vladimirovich Akimov.

G.V Akimov was born in 1901 in the family of a teacher at a trade institute. On finishing his secondary education in 1915, G.V. Akimov entered the Physical-Mathematical Faculty of Moscow State University. However circumstances at that time did not allow G.V. Akimov to continue his education. As a 17-year old youth he entered the ranks of the Red Army as a volunteer and took an active part in the Civil War. While he was still in the Red Army, in March 1920, Georgy Vladimirovich entered the ranks of the Communist Party and tirelessly served the cause of the Party until the last days of his life. At the end of the Civil War Georgy Vladimirovich was demobilized in order that he might continue his education at the Moscow Higher Technical Institute in the Chemical faculty, and he began to specialize in metallurgy and treatment of metals. In 1926, G.V. Akimov graduated from the Chemical Faculty of the MYTU, receiving the degree of Engineer-Technologist, and began his scientific and engineering work in the aviation industry, which at that time was not only founded. Our country was faced with the problem of mastering and creating new corrosion resistant light alloys, stainless and heat-resistant steels required for aeroplanes and other engines. Georgy Vladimirovich ardently undertook the solution of these problems.

G.V. Akimov founded the first laboratory specializing in corrosion and carried out deep theoretical and practical investigations on metal corrosion. Even the early work of G.V. Akimov was noted for its scientific depth, its originality and for its great practical importance. The following are the most important investigations which he carried out in 1927-1932: A study of the corrosion behavior of duralumin in contact with other metals; a method for the protection of aluminum alloys with the aid of protectors; the study of the corrosion behavior of riveted seams and the establishing of suitable composition of rivets; the protection of aluminum alloys with the aid of metallization, etc.

In 1927 G.V. Akimov discovered and explained the protective action of zinc on aluminum and its alloys, although in the literature of the time it was held that such a protection was not possible. In the same year, discussing results obtained on metallic contacts, G.V.Akimov arrived at the concept of multielectrode systems. In 1928, G.V. Akimov wrote the monograph "Metals and Alloys in Chemical Plant Construction", which for a long time was the only guide on the corrosion behavior of metallic materials.

In 1929-1931 G.V. Akimov carried out a series of researches on stainless steels and developed new steels. The range of his scientific researches was constantly widening.

In 1931, G.V. Akimov, for the first time, organized a Department of Metal Corrosion in the Moscow Institute of Non-Ferrous Metals and he gave the first lectures in the course.

In 1933-38 Georgy Vladimirovich undertook the wide development of the theory of multielectrode systems, the elucidation of the loss in corrosion processes with oxygen and hydrogen depolarization, the study of non-equilibrium electrode potentials of pure metals insolid solution. The results of these researches were given to a series of conferences and published, both as articles and as individual monographs.

As a result of the scientific and pedagogic activity of G.V. Akimov, a school of Soviet corrosion specialists, the largest in the world, has been founded.

In 1939, G.V. Akimov was elected a corresponding member of the Academy of Sciences, USSR. From that time, as well as carrying out his work in the aviation industry, G.V. Akimov guided the work on metal corrosion in the Institute of Physical Chemistry, Acad. Sci. USSR. An outstanding feature of the laboratories founded by G.V. Akimov was their close and indissoluble connection with industry, which permitted them to put the latest scientific advances into practice. In 1947, G.V. Akimov organized a commission on the prevention of metal corrosion under the Division of Chemical Sciences Acad. Sci. USSR and this carried out fruitful work under his leadership and direction—the work on the prevention of metal corrosion in our country. Under his guidance a network of corrosion stations was organized in the USSR and a number of important problems was solved.

From 1949 until his death, G. V. Akimov was Director of the Institute of Physical Chemistry Acad. Sci. USSR and at the same time he continued to direct the Division of Corrosion of the same Institute as well as the VIAM Laboratories. From that time G.V. Akimov was a member of the Editorial Committee of the Journal of Physical Chemistry. The scientific activity of G.V. Akimov was many-sided. His fundamental investigations in the field of metal corrosion are well known; among them the following may be specially mentioned :

1) Work on the irreversible electrode potentials of metals of importance in the theory of corrosion. In this work the importance of non-equilibrium potentials in corrosion processes was first shown and an extremely large amount of experimental material was obtained and the theory of irreversible potential developed.

2) Work on the theory of multielectrode galvanic systems and their application to corrosion problems. The concept of corroding metals as multielectrode systems was first put forward by G.V.Amikov in 1927.

In recent years, G.V. Akimov and his students completed the development of the theory of multielectrode systems and this permitted the solution of very important theoretical and practical problems in the corrosion of complex metallic systems.

3) Work on the study of the electrochemical properties of protective films in which the connection between protective films and electrochemical factors (the existence of anode, cathode and inert areas) was first shown. In this work, it was also unambiguously shown that there was a connection between the passsivity of stainless steels and protective films.

4) Work on the mechanism of the corrosion process. G.V. Akimov and his school made an especially large contribution in the field of corrosion processes with oxygen depolarization. As is known, these processes include the most important technical cases of aluminum and iron corrosion. Here new relationships were discovered and explained; for example, the nature of the connection between the corrosion current and the cathode area: the dependence of the corrosion current over a wide range on changes in the ohmic resistance, the initial electrode potential and anode area.

5) Work on the study of microgalvanic elements in which, with the aid of refined methods of investigation on actual structure components of alloys, the quantitative confirmation of the microelement hypothesis was obtained.

6) Work on the electrochemical and corrosion behavior of metals and alloys in oxidation.

G.V. Akimov was also widely known for his work in the field of the physical chemistry of metals. He published a number of papers on the internal transformations and the technological properties of stainless steels, which played an important part in the development of stainless steel production in the USSR. He directed work in the field of physical methods for the study of metals, including the field of electron microscopy and ultrasonic defectoscopy of heat-stable alloys, steels and aluminum alloys.

The Theoretical work of G. V. Akimov enabled him to solve a number of practical problems, of which the following are the most important:

(1) the development of new methods for the protection of aluminum alloys;

(2) the development of methods for the protection of construction work;

(3) the development of methods for the prevention of gas corrosion;

(4) the development of new methods for the physical chemical study of metals.

G.V. Akimov published about 200 scientific papers. In addition to these scientific papers, he wrote 5 monographs and one textbook. Of these, his book "Theory and Methods of Investigation of Metal Corrosion" was awarded a Stalin prize. For his outstanding work in the study of the electrochemical protection of films Georgy Vladimirovich was awarded the D.I. Mendeleev prize in 1952.

For his fruitful scientific work G.V. Akimov was twice decorated by the Government with the Order of Lenin, with the Order of the Red Banner of Labor and was three times awarded the Stalin prize. He was also made an Honored Worker in Science and Technology.

The progressive Soviet Scientist-Communist, G.V.Akimov, succeeded in skillfully combining deep theoretical studies with the solution of practical problems. G.V. Akimov selflessly gave of his strength and his knowledge for the benefit of our great motherland. The memory of Georgy Vladimirovich, an outstanding patriot of our country, will always be preserved in the history of our national science.

CHRONICLE

DIVISION OF CHEMICAL SCIENCES, ACADEMY OF SCIENCES USSR

A general meeting of the Division was held on March 27th,1953, at which Acad. M. M. Dubinin, Division Acadamecian-Secretary, reported on the work of the Division. At the same meeting a new Bureau was elected. Members of the Division and also members of the scientific administrative staffs of chemical institutes took part in the meeting.

In his address, Acad. M. M. Dubinin said that the most important activity of the Division was the directing of the institutions which were placed under its control. This was effected by developing, in co-operation with institutes of the Division, future plans for the development of chemical science within the framework of the Academy of Sciences; by laying down the direction scientific work should take and the set-up of institutes; by combining yearly plans of institutions in the Division and approving working plans. The Division checked the fulfilment of plans for scientific work and received the yearly reports of institutes on their scientific work. The work of the Division also included the organization of research on complex scientific problems and the coordination of the activities of chemical institutions, Republican Academies of Science, and branches of the Union Academy. In the work of the Division, great attention was paid to the introduction of the results of completed scientific work into the country's national industry.

In addition, the scientific work of the Division included the organization of conferences, discussions and general meetings, the direction of the work of Division Commissions, the general direction of chemical journals published by the Academy of Sciences, and of publications of both Commissions and Institutes. The training of personnel for the Institutes and the control of personnel also came under the Division. From this it could be seen — the speaker pointed out — how wide and diverse were the functions of the Division.

Turning to the question of the organization of new institutions and the development of scientific research, Acad. Dubinin said that in recent years a number of new research institutions had been set up within the framework of the Division; these included: The Institute of Silicate Chemistry and The Institute of High-Molecular-Weight Compounds (in 1948). The structure of existing institutes had been changed, and in this reorganization a number of new laboratories had been set up.

Over a period of three years new commissions had been formed; these included: The Commission for the Development of the Scientific Heritage and Publication of the Works of A.M. Butlerov and the Commission for Chromatography. In addition, several commisions, the activities of which were valueless, were abolished.

In the Division Institutes research work on a number of new problems was taken up; these included problems on the theory of chemical structure and reactivity, on high-molecular-weight compounds, on silicate chemistry etc. Research on organo-element compounds made significant progress; work on the synthesis of heavy organic chemicals, on analytical chemistry, on corrosion, on kinetics and on adsorption was greatly extended. The most modern methods such as X-ray structural analysis, electron miscroscopy etc. were more widely used.

The Division Bureau paid great attention to the making of plans for the development of chemical sciences in the Academy organization so as to fulfil the decisions of the XIX Congress of the Communist Party of the Soviet Union. The historic task set by the XIX Congress for the further development of progressive Soviet Science so that it should occupy the first place in world science has inspired the members of the Division. The leaders concerned had shown great creative team-work in the presentation of reports on various branches of chemistry.

Turning to the question of the introduction of completed scientific work into national industry, the speaker pointed out that in recent years the bonds between the chemical institutes of the Academy and industrial undertakings and Ministerial research and planning organizations had been greatly extended and strengthened. A polular movement had developed in our country with the slogan of socialist cooperation between workers in science and industry, and its influence was felt on the work of the Academy chemical institutes.

In 1951 the total number of agreements on cooperation entered into by institutes of the division amounted to about 70, but in 1952, according to incomplete figures, it exceeded 150. Most of the agreements relate to the following institutes: IOKh (Institute of Organic Chemistry), 46; IKhS (Institute of Silicate Chemistry), 32; IONKh (Institute of General and Inorganic Chemistry), 27; IFKh (Institute of Physical Chemistry), 25.

In 1951 the chemical institutes of the Division introduced a total of 25 projects, and 23 in 1952. In 1951 the introduction of 15 projects was completed; in 1952, 8 were completed and 5 were tested with good results on the factory and pilot-plant scale, i.e., a total of 13.

Acad. Dubinin then dwelt on the nature of the more important projects introduced into industry. A number of important projects in the chemical institutes were at the introduction stage.

The speaker then remarked that in addition to the projects introduced by the institutes, there were also projects which were worked out and introduced in industry in consultation with the Academy's institutes. The work of IONKh and the Hydrochemical Institute on the investigation of soil salinity and salt deposits on canal routes and on the hydrochemical investigation of rivers and other water routes was of great importance.

However, by way of self-criticism, remarked Acad. Dubinin, — the number of projects introduced their importance in the national economy and the rate of their development were far from satisfactory, and we could not be satisfied with them. The reasons for this lay in lack of clarity of purpose and weak organization in the work of the Division, and of the Academy as a whole, in introducing completed projects. Instead of maintaining close contact with industrial organizations at the stage of laboratory investigations, when corrections and modifications could be introduced, our institutes only turn to industry when the basic work has been concluded; it frequently happens that some essential features of the process have not been fully dealt with and this leads to differences of opinion as to whether the process is ready to be introduced. Another cause of the difficulties is to be found in the lack of enthusiasm among industrial workers for the introduction of Academy of Sciences projects.

Socialist cooperation permits the union of the forces of the Academy institutes with those of industry at the earliest stages; these forces can work out the technological conditions, make an authoritative examination of the raw material, plant and economic problems and both sides can show a full development of initiative. The early cooperation of Academy institutes with industrial research and planning institutes can be especially fruitful. In this connection some Academy institutes should be strengthened by the addition of chemical technologists to the staff.

It is necessary that the forces of the institutes should be mobilized for the all-round increase in the rate of introducing new projects and for strengthening our bonds with industry; the main forces should be concentrated on the solution of large and important problems of the national economy, leaving the secondary and less important problems to factories, laboratories, and high-school departments.

Acad. Dubinin then dealt with the important field covering cooperation in scientific research between institutes of the Academy of Sciences, USSR, and Academies of the Republics. A great part in cooperation was played by visiting sessions held in conjunction with Republican Academies. Recently the Division of Chemical Sciences held four joint visiting sessions: with the Latvian SSR Academy of Sciences, with the Georgian, with the Ukrainain, and with the Uzbek SSR Academy of Sciences. It should be mentioned that each succeeding session was an improvement on the previous one. Thus, during the last joint session in Tashkent, conferences were organized dealing with all the main projects of the Division institutes. This was of no small significance for the coordination of scientific research.

The joint sessions were important events in the scientific life of the republics. As a rule they aroused great interest in the part of the governments of the republics, party organs and the chemical fraternity.

In spite of some deficiencies and irregularities, the work of coordination made definite progress; as a result there was a marked movement in the chemical institutes of the Republican Academies toward the concentration of forces and resources on the solution of fundamental tasks, appropriate to the scientific set-up of each particular institute.

The Bureau of the Division received and discussed the reports of the directors of independent chemical institutes, for example of the former Tadzhik branch, and of the Crimean and Kirgiz branches.

During the last two years the methods of coordination between the personnel of Republican Academies had been perfected. In 1951 coordination was achieved through special sessions of the Division; in 1952 (in practic at the beginning of 1953) through the Division institutes working on individual problems with confirmation of decisions by a plenum having the character of an enlarged Division Bureau.

The main deficiencies in this complex work were due to the tardy reviewing of work and examination of the plans of coordinating centers and institutes. Several reviewers gave superficial and vague decisions. The organization of cooperative work left much to be desired. In the main, coordination amounted to correcting and improving the working plans of institutes, and in particular in excluding the less important work, and in indicating desirable directions in which chemical research might be carried out. However, big, fundamental changes in institute plans were not achieved. Therefore, the plans of the Chemical Division and those of the chemical institutes of the Republican Academies of Sciences and of the branches cannot be considered as comprising a unified plan.

A decided improvement is need in coordination to do away with awkward multiple plans, and to replace them by a single plan for the development of chemical sciences, with the Academy system as a basis for coordination.

Turning to the question of the arrangements for sessions, conferences and meetings of the Division, the speaker first remarked that the idea of general meetings of the Division was to provide an opportunity for making scientific contacts in the discussion of papers on important theoretical research of general interest. The main aim in presenting the papers was to develop discussions, because critical examination promotes the formulation of more correct ideas. Many chemists from various scientific and higher educational institutions were invited to the meetings.

In the last three years 26 session of the division were held, consisting of 50 meetings with 114 papers. Of these, 12 meetings were held in connection with the anniversaries of great events in the history of national science.

During this period, members of the Division presented 55 papers at the regular meetings; and Science Fellows at the Academy of Sciences chemical institutes, about 30 papers. Scientists from other research institutions also presented papers; these included: A.V. Kirsanov, 4 papers (Dnepropetrovsk Metallurgical Institute), K. P. Mishchenko (Leningrad Technological Institute), I. N. Plaksin (Institute of Mining, Acad. Sci. USSR); M.L. Chepelevetsky (NIUIF); A.N. Pudovik (Kazan Branch), S.V. Kaftanov, G.S. Zhdanov (Karpov Institute) A.I. Kiprianov, Ya.N. Fialkov, E. A. Shilov, V. A. Reiter (Academy of Sciences, Ukr. SSR); R. Ya Levina, N.I. Gavrilov (Moscow State Univ.); Yu. G. Mamedaliev (Academy of Sciences, Azerbaidzh. SSR), and others; in all, 20 papers were presented.

The attendance of Division members at regular meetings was not high. In the period 1949-1952 several members did not present even a single paper at regular meetings.

Conferences and congresses on special branches of science, usually on one theme, are an important part of the Division's scientific activity. Conferences at which the full text of papers was first published were the most complete. The presentation of the paper took ten minutes and about 70% of the available time was occupied by the discussion. Here the work of the Commission on High-Molecular-Weight Compounds deserves special mention.

The Division held the following conferences and congresses:

In 1949 Conference on Gas Analysis (Commission on Analytical Chemistry); Conference on High-Molecular Weight Compounds, devoted to general questions on the chemistry and physical chemistry of high-molecular-weight compounds; Conference on the Scientific and Technical Application of Photography and Cinematography.

In 1950: Second All-Union Conference on Physico-chemical Analysis; All-Union Conference on Microelements. Conferences on: Electrochemistry, Chromatography, Chemistry of Complex Compounds, Stainless Steels, Color Photography and Cinematography, The Molecular Weight of Polymers, Electrochemical Methods of Analysis. Fourth Congress on Hydrochemistry (Novocherkask).

In 1951: The All-Union Congresses on the Theory of Chemical Structure, On Metal Corrosion in Sea Waters of the Caspian Basin (Baku), On Fundamental Problems of Scientific Photography (Odessa); The Second All-Union Congress on the History of Native Chemistry (Leningrad); Congress on Classical Methods of Chemical Analysis and Congress on the Technique of Cinematography, Sensitometry, and the Application of Cinematography to Medicine (Leningrad).

In 1952: Discussion-Conference on the Principle of the Trans-Effect and on Metal Alloys (IONKh, Acad. Sci. USSR); Conferences on the Theory of Ion Exchange, Synthesis and Application of Ion-Exchange Materials (jointly with the Commission on Vapor of High Parameters), and the Seventh Conference on the Chemistry and Physical Chemistry of High-Molecular Weight Compounds (Leningrad).

In carrying out the decisions of the All-Union Congress on the Theory of Chemical Structure (1951), two special congresses were held: In Erevan — on the relation between chemical structure and pharmacological activity; and in Kiev — on the mechanism of organic reactions. The decisions of all conferences and congresses were discussed and confirmed by the members of the Division Bureau. In 1953, it is proposed that a symposium be held on chemical kinetics. In the future, the Division Bureau must pay more attention to improving the subject-matter and the organization of conferences, making them more influential, and having the most timely topics discussed.

Turning to the activities of the Division in connection with the directing of chemical journals, Acad. Dubinin made a number of criticisms. During the past few years much work had been done in reviewing the composition of editorial committees. In particular the principle of having the same member sitting on several different editorial committees—previously a common practice—was changed. The new editorial committees were made up of scientists who could take an active part in the life of the journal, i.e., referee the papers, maintain a punctual attendance and participate in the meetings of the committee.

There were a number of deficiencies in the editorial work of chemical journals, which had not been made good even now, although they had been pointed out to the editors when their reports had been considered by the Division Bureau, and instructions had been issued. In the first place the complaint relates to the publication of discussions of the basic problems of chemistry. The publication of discussions was particularly poor in the Journal of General Chemistry, The Journal of Applied Chemistry, and The Colloid Journal. The Editors adopted a policy of laissez-faire toward the supply of papers. The Editorial Committees did not organize the presentation of papers on most important fundamental questions in different branches of chemistry. Papers published in some journals have been of poor quality scientifically.

In some journals there is a lack of esprit de corps in the work and not all members of the committee are called upon to referee papers. There is a long delay in having papers refereed. The attendance of some members is unsatisfactory.

Another deficiency in editorial work is the long delay in the publication of papers, which is sometimes as much as two years after they have been sent in. The Division constantly points out to editors that they should reduce the length of papers in editing and also make greater use of small type. However, these measures alone will not be sufficient—the portfolio of papers held by many journals still remains large, amounting to a two-years run (Journal of General Chemistry, Journal of Applied Chemistry, Journal of Analytical Chemistry); the volume of a number of journals must therefore be increased or some other radical measures taken.

The Division increased the volume of three journals since 1952; the Bull. Acad. Sci. USSR, Div. Chem. Sci. was increased by 30 printed sheets in a year (from 7 to 12 sheets per number); the journal Progress in Chemistry was doubled in size (12 instead of 6 numbers per year); the Journal of Physical Chemistry was increased by 24 sheets per year (from 8 to 10 sheets per number). In order to relieve the editorial portfolio of the Journal of General Chemistry, the Praesidium the Academy of Sciences USSR had decided to issue as a supplement to the journal, requiring separate payment, two collections of papers amounting to over 100 printed sheets.

The question of relieving the congestion in the Journal of Applied Chemistry and in the Journal of Analytical Chemistry has not yet been resolved.

The work of editors and editorial committees demanded of them more serious consideration of the essentials of their business in connection with the making of radical decisions to improve the lay-out of the journals and take measures to ensure that papers would be published not later than 6 months after receipt.

Academician Dubinin then dwelt at length on the selection, education, training and assignment of scientific personnel. He quoted numerous examples of poor work in dealing with personnel problems in several institutes.

In many institutions of the Division, self-criticism in the work of the directorate, academic councils and colloquims continued at a low level. Criticism and self-criticism had still not become fundamental methods by means of which errors and deficiencies in scientific work could be detected and overcome. One of the causes of the unsatisfactory position in the development of criticism and self-criticism in institutions of the Division, as had been justly noted at meetings of the more active members, was the passive attitude of a number of members of the academic councils of some institutes, among which should be mentioned, the Institute of Chemical Physics, The Institute of General and Inorganic Chemistry, and the Institute of Organic Chemistry.

In this connection it should be mentioned that criticism and self-criticism was not sufficiently developed in the work of the Division Bureau itself, where the lack of activity of a number of members had been observed.

Neither did the directors reports on the recent meetings on personnel contain sufficient self-criticism. Thus, for example, in the report of the director of the Institute of General and Inorganic Chemistry, Corr. Member of the Academy of Sciences, USSR, I. V. Tananaev, there were no concrete proposals for the development of criticism and self-criticism at the institute; the report of the director of the Institute of Organic Chemistry, Prof. V.V. Korshak, also showed similar deficiencies.

In all institutes the work of training personnel through post-graduate and doctorate courses was far from satisfactory, and also the training of staff personnel. Thus, for example, in 1952 the Institute of High-Molecular-

Weight Compounds did not produce one Candidate in Science from their modest number of post graduate students. During the existence of this institute, not a single Candidate's or Doctor's dissertation had been presented by its Fellows, although the demand for qualified personnel in this institute is keenly felt. It should be mentioned that the leaders and laboratory directors of this institute have not paid proper attention to initiating young workers to post-graduate work, and they have taken no measures to organize the preparation of highly qualified workers by means doctorate courses.

Such a large institute as the Institute of Physical Chemistry planned to have 6 post-graduate students present Candidates' dissertations in 1952. However only one student presented his dissertation within the required period; the remaining five were long delayed. Moreover, in 1952 two students left the Institute of Physical Chemistry without presenting Candidates' dissertations, and three without presenting Doctors'.

During the whole of the existence of the Laboratory of Peroxide Compounds, not a single Candidate received his degree on the basic work of the laboratory - the synthesis of peroxides. Drs. Chem. Sci. S.Z. Makarov and V.I. Mikheeva have not given sufficient attention to post-graduate work.

Of 7 post-graduate students passing out from the Institute of General and Inorganic Chemistry in 1952, one presented his dissertation in time and the others were 1 to 9½ months late. In the past year, in this large institute, only 4 students were accepted for post-graduate work: in addition one took up post-graduate work without giving up his main work; this is entirely unsatisfactory. This institute has a number of leading workers— Drs. Chem. Sci. M.M. Yakshin, A.M. Rubenshtein, A.D. Gelman, A.V. Babaeva, V.G. Tronev, V.I. Goremykin and others— who pay insufficient attention to the training of scientific workers. The institute does not make proper use of its highly qualified personnel for the training of future Doctors of Science.

Serious deficiencies in training through post graduate work and doctorates also occur in the Institute of Chemical Physics, where the scientific leaders pay insufficient attention to post-graduate work, which as a rule is not carried out in the time required. Several leaders (Corr. Mem. Acad. Sci. USSR V.N. Kondratyev, I.L. Zelmanov) entrust post-graduate students to other persons. Only one student presented a dissertation in the IKhF high-voltage section during the last few years.

A number of similar deficiencies in the development of personnel also occurs in the Institute of Geochemistry and Analytical Chemistry, and also in the Institute of Silicate Chemistry.

Affairs are somewhat better in the Institute of Organic Chemistry; however, here also only 80% of the Candidates -students presented their dissertations within the required period. Some leaders (Dr. Phys., Math., Sci., A.I. Kitaigorodsky, Dr. Chem. Sci. A.E. Borisove, Corr mem. I.N. Nazarov and others) did not present their students in time. During a long period of work at the IOKh, a Corr Mem. I.V. Obreimov and Dr. Chem. Sc. A.M. Rubenshtein did not present a single post-graduate student. The Laboratory for Intermediates and Dyes, directed by I.V. Obreimov has had no post-graduate students up to now. A number of leading Fellows (Corr. mem. I.V. Obreimov, Acad. B.A. Kazansky, Corr. mem. I.L. Knunyants and others) have not paid due attention to the preparation of students for the doctorate.

There are also material defects in the Division institutes in the training of staffs. In some institutes due attention is not given to politico-ideological work among the leading workers, especially such forms of political preparation as participation in the University of Marxism-Leninism. Thus, for example, during the entire period of existence of the Institute of High-Molecular-Weight Compounds, no Fellow with a science degree has graduated from the University of Marxism-Leninism. In the Institute of Physical Chemistry none of the leading workers is studying the University of Marxism-Leninism courses.

Concluding this part of his report, Acad. Dubinin mentioned some concrete measures for improving the work of educating and training of scientific personnel. Acad. Dubinin closed his report with the following words:

> "May I express my confidence that the development of genuine business-like and sound criticism in the spirit of the instruction of the XIX Congress of the Communist Party of the Soviet Union will promote the improvement of the work of the Division of Chemical Sciences in all its branches."

After the report of the Academician-Secretary of the Division, Acad. Dubinin, the meeting was opened to discussion; several Academicians, Corresponding Members, and Scientific Fellows of the Division Institutes took part in the discussion.

In the discussion of Academician Dubinin's report there took part: Academicians G.G. Urazov, and P.A. Rebinder, Corresponding Members N.A. Izgaryshev, S.N. Danilov, A.D. Petrov, A.F. Kapustinsky, N.I. Nikitin, A.P. Vinogradov, I.A. Kazarnovsky, V.I. Spitsyn as well as Fellows of the institutes.

At the same meeting a new Division Bureau was elected composed of the following: Academicians N.N. Semenov and A.V. Topchiev, Corresponding Members A.P. Vinogradov, S.N. Danilov, I.L. Knunyants, V.I. Spitsyn, I.V. Tananaev, Doctors of Chemical Sciences N.I. Shuikin and K.T. Poroshin.

CONFERENCE ON CHEMISTRY OF THE BORATES

On October 23 and 24,1952, a conference on the chemistry of the borates was held in the Institute of Chemistry of the Latvian SSR Academy of Sciences in Riga. About 100 people participated in the work of the conference. The first day was devoted to theoretical, and the second to practical problems of borate chemistry.

Opening the Conference, the Director of the Institute, A.F. Ievinsh, pointed out that although boron as an element was known for about 150 years and several of its compounds were used in ancient times, the chemistry of boron compounds had been poorly studied. To-day boron was of great practical importance. Boron was in demand not only in the chemical and other industries but also in agriculture.

In the Institute of Chemistry of the Latvian SSR Academy of Sciences work on the chemistry of the borates was carried on by a small group of workers. This work had led to the synthesis of a number of new borates. Work in the same field was being carried on in other research institutesin the Soviet Union. It therefore seemed useful to hold a conference on the chemistry of boron in order to discuss the results obtained in recent work and to exchange information so that the direction of further work in this field should be marked out. Moreover, such a conference would enable personal contacts between scientists to be strengthened and this was of great value.

The first speaker, A.D. Keshan (Institute of Chemistry, Acad. Sci. LSSR) in his paper "Problems of Borate Chemistry" considered as the main problem the extension of the sources of boron compounds by utilizing natural brines and industrial effluents which contain small quantites of boron together with large quantities of other salts. For the solution of this difficult task a detailed knowledge of boron chemistry was needed. But our knowledge in this field is still meager and superficial. During the last two decades, Soviet chemists have done much in the field of borate chemistry. The boron minerals of the Indersk deposits had been studied; A.V. Nikolaev had developed the well-known field method of investigationg boron minerals; the nature of borate re-arrangement on heating had been discovered and investigated; in co-operation with A.G. Kurnakov and N.M. Selivanova a number of natural borates had been synthesized and also several artificial borates.

In the Institute of Chemistry of the Latvian SSR Academy of Sciences, work had been carried on since 1947 on the synthesis of heavy metal borates. About 20 borates had been obtained and the methods of preparing others had been improved.

Little had been done up to now on the structure of borates. Even for such a well-known and comparatively simple compound as borax, different workers had proposed four different structures. The synthetic borates of the divalent heavy metals provided valuable material for the application of methods of studying structures— electrical conductivity, cryoscopy and X-ray analysis. Whatever the method used for extracting boron—precipitation, coprecipitation, sorption or selective ion-exchange with anionites— a knowledge of the fundamentals of the process was essential for success. Therefore, in addition to applied work it was necessary to carry on theoretical work on the chemistry of the borates.

G.K. Gode (Instituteof Chemistry, Acad. Sci. LSSR) in his paper "The Synthesis of Borates in Aqueous Solution" pointed out the importance of several factors, such as: the composition of the precipitating reagent, the proportions and concentrations of the starting materials. In the exchange reaction with equivalent quantities of borax and calcium chloride in the solid phase, calcium tetraborate was not obtained but a precipitate with a ratio of B_2O_3: CaO = 1.6; but in the liquid phase the ratio was 2.4. Here there is a step-wise change in the pH of the liquid phase. If the precipitating reagent is chosen with a pH corresponding to the constitution of the borate being prepared, the amorphous precipitate which separates at first crystallizes fairly rapidly. From a mixture of borax and sodium hydroxide at pH 11, the diborates of Ca, Sr and Ba crystallize out in 1-2 hours. From a mixture of borax and boric acid, the same elements give crystalline hexaborates after several days. A considerable excess of reagent is always necessary; the excess acts as a buffer in stabilizing the pH of solution. Amorphous precipitates of heavy metals, obtained by precipitation of borax solutions, are converted to crystalline higher borates after several days in boric acid, for all borates are very soluble in boric acid.

A.G. Kurnakova (Institute of General and Inorganic Chemistry, Acad. Sci. SSR) reported on the results of studies of ternary and quaternary systems with boric acid and the oxides of calcium, magnesium, sodium, and potassium as components in aqueous solution at 25°.

The study of these systems was intended to throw light on the origin and conditions for the mutual transformation of the boron minerals in the Indersk deposits. Both natural inonite, inderite, borosodocalcite, inderborite and synthetic borates had been obtained with different ratios of B_2O_3: RO It was notable that in the systems examined, none of the slightly soluble borate compounds, the native borates, for example colemanite, askarite, hydroboracite etc., the main minerals in the Indersk deposits, were obtained. Thus, of the calcium borates, instead of the sparingly soluble pandermite $4CaO \cdot 5B_2O_3 \cdot 15H_2O$ and colemanite, $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, the more soluble native borate, inonite, $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, was obtained. Of the magnesium borates, instead of askarite, $2MgO \cdot B_2O_3 \cdot H_2O$, the principal Indersk mineral, the more easily-soluble inderite, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$.

Most of the native borates obtained in the studies of these systems were metastable compounds. In nature under the corresponding conditions they are converted over a long period into less hydrated and less soluble stable forms— colemanite, pandermite, ascharite and hydroboracite.

Ya.Ya. Yarzhemsky (All-Union Geological Research Institute) reported on the geological structure of the Indersk borate deposits and on the nature of the raw materials available for conversion into boric acid and borax.

M.G. Valyashko (VNIIG) reported on coprecipitation of boric acid from the liquors obtained in the preparation of boric acid from boron minerals. These liquors contain 1 to 2% of boric acid. About 90% of the boric acid could be co-precipitated with magnesium hydroxide. The precipitate was, however, difficult to filter and its B_2O_3 content was low.

L.E. Berlin (NIUIF) reported on the use of manganese, calcium and magnesium to precipitate boric acid from the mother liquors obtained in the production of boric acid. He had studied the solubility of manganese borates of different compositions in water and in solutions of boric acid, borax, magnesium sulfate and sodium chloride at 25°. In water the manganese borates are hydrolyzed and the hydrolysis increases with time. The manganese borate which tended to decompose least was the one having the ratio B_2O_3 : MnO ≈ 1, obtained by precipitation from alkaline solution. The results obtained were applied on the technological scale. After manganese sulfate had been added, the solution was neutralized with calcium or magnesium oxide. After the precipitation the liquid phase contained 0.37-0.60% of B_2O_3. Studies were also carried out on the precipitation of boric acid from these solutions with the aid of small quantities of MgO. It was then found that 90% of the B_2O_3 in the initial solution passes to the precipitate. The results were tested on the production scale.

K.G. Gode (Institute of Chemistry Acad. Sci. LSSR) reported on the extraction of boric acid from dilute solutions with the aid of calcium chloride and magnesium chloride and also by ion exchange. For the precipitation with calcium chloride the best pH was 9.5; after the precipitation the liquid phase then contained 0.25% B_2O_3. The bulk of the calcium borate is precipitated in 24 hours. When calcium chloride is replaced by magnesium chloride, the precipitate settles more slowly over 28-35 days. 0.3% of B_2O_3 is retained in the liquid phase.

Only pure solutions of boric acid had been used up to now in the experiments with ionites. Types MMG, MG, TH and H had been tried. Up to 90% of the boric acid was absorbed by ionites after several days under static conditions from solutions containing 0.2% B_2O_3; the B_2O_3 content of the liquid phase falls to 0.02 - 0.03%. The ionite must be regenerated with sodium hydroxide. The action of ionites on salt solutions has not yet been tried.

Research Student V.V. Khadorchenko (Riga) reported the results of studies on the ternary system "copper hydroxide - boric acid - water" at room temperature. The reaction between copper hydroxide and boric acid is slow; after 45 minutes certain types of compund were obtained and different types after 115 days. These compounds were insoluble in water and were not decomposed by prolonged boiling, but they were easily decomposed by acids and by ammonia solution. After precipitation several hundredths of a per cent of B_2O_3 remained in solution. Perhaps this effect might be used for extracting boric acid from dilute solutions.

Opening the discussion on the papers, Acad. G.G. Urazov pointed out that the necessity of having boron compounds to meet the needs of the National Economy meant that a constant search must be made for new ways of utilizing native resources, and for this a knowledge of boron chemistry was of first importance. The chemistry of boron was being studied in the Institute of Chemistry of the Acad. Sci. LSSR. Here the complexity of the conditions for the synthesis of borates had been shown: the important role of pH, the increase in acidity of the liquid phase in exchange reactions and other conditions When the right conditions had been found, sometimes only hours or days instead of weeks or months were required to prepar crystalline borates. The study of borate chemistry should be two-sided— from the point of view of their formation and occurrence in nature and from the point of view of their utilization. A scientific co-ordinating center should be set up to unite and direct the work of scientific institutions.

Corr Mem. Acad. Sci. USSR A. S. Grinberg pointed out that the work carried out in the Chemical Institute of the Acad. Sci. LSSR was interesting not only in relation to borates but also to other inorganic compounds, for example, the ferrophosphates. It was often contended that preparative chemistry was becoming obsolete. But only the harmonious integration of different methods with due regard to technical applications and precise analysis would give the required results.

Corr. Mem. Acad. Sci. LSSR, L.K. Lepin expressed the opinion that many of the speakers had exaggerated the part played by the pH of the liquid phase in the synthesis of borates. From the papers it was clear that the liquid and solid phases were not in equilibrium. An increase in the acidity of the liquid phase leads to the formation of polyborate anions. This process should be studied in detail with the aid of potentiometric titrations, these being carried out over several days and weeks so that equilibrium could be established between the liquid and solid phases. On long contact of the solid and liquid phases during the exchange reactions of solid borates with salts of the heavy metals both phases should tend toward equilibrium, and these changes should be followed over a period.

G.B. Romov (Aktyubinsk Chem.Combine)remarked that the demand for boric acid increased from year to year, while the methods of utilizing the raw materials improved only slowly. The effluent losses were still high. There were a number of unsolved problems in the technology of production which was already on a proper basis, and where the solution systems used had been well studied. In the crystallization of boric acid it is desirable to cool the solutions to the lowest possible temperature, but then a low-quality product was sometimes obtained because of the high content of magnesium sulfate and other impurities in the solutions. The possibility of extracting boron from dilute solutions should be further studied, as this was demanded by considerations of national economy.

M.G. Valyashko - a representative of the producers - said that considerable quantities of boron were lost in effluents. Necessity compelled us to pay close attention to boron. Here, several methods for extracting small quantities of boron had been discussed. But it was desirable that we should know the economic side of these methods. It was not known if it is possible to use cobalt, nickel, zinc, and copper in the extraction of boron. The most promising of these are the magnesium compounds which are also the cheapest at present.

L.E. Berlin acknowledged the successes in synthesizing new borates, but this work, in his opinion, did not lead in the proper direction. Borates were obtained with expensive cations: nickel, cobalt, lead, copper. It was not known if they could be used because of this. Problems of practical importance should be developed. The report on the copper borates was interesting, but it was impossible to wait 45 or 115 days for their precipitation; ways of shortening the time should be found. Besides this process could be used only where cheap copper residues were available. In selecting a collector two factors should be taken into account; insolubility of the compounds and the economic effect. Magnesium was the most economical. Collaborative work should be carried out on the study, precipitation and extraction of boron from the precipitates obtained.

K.M. Saldadze (All-Union Reagent Research Institute) remarked that much interesting material on the chemistry of boron had been heard at this conference. The representatives of the Institute of Chemistry of the Acad. Sci. LSSR had shown that they correctly interpreted the instructions of the XIX Party Congress, "To develop technical problems on a scientific basis". A defect was the little attention paid to the economics of borate production. From other papers it was clear that great attention had been given to the working of minerals and the utilization of works liquors and natural waters, but nothing had been said about the technical production of boric acid and its salts of reagent purity, issued in large quantities for analytical and other purposes. The technique of determining small quantities of boron present as an impurity in various compounds had also not been dealt with... Precipitation of boron from solution was a more promising method of extraction than the method using ion-exchange resins. All the resins reacting with boric acid, which had been tried up to the present also adsorbed anions of other acids. Selective anion exchange resins should be obtained and also solid amines. The All-Union Reagent Research Institute was carrying out work in this direction. Insoluble amines had already been synthesized which absorb silicic, carbonic and other weak acids. These amines could problably be applied to the extraction of boron from borate waters.

RESOLUTION

As a result of the papers read and the lively exchange of views which followed, the conference reports:

1. The Conference organized by the Institute of Chemistry of the Acad. Sci. LSSR consists in a meeting of the representatives of many institutions engaged in problems of borate chemistry and the utilization of borates to satisfy the needs of the national economy.

2. As a result of the work done in the country's research institutes, a number of systems of B_2O_3 have been studied, studies have been carried out on the synthesis of a number of new borates, on methods of precipitation, on co-precipitation and adsorption of boric acid; new technical processes for the treatment of borate raw materials have been worked out; several geochemical problems have been studied.

3. This work, which gave results of practical and theoretical value, was carried out without sufficient co-ordination. In view of this, it is the opinion of the Conference that a co-ordinating center should be organized under the Praesidium of the Academy of Sciences, USSR

4. The Conference is of opinion that further work on the chemistry and utilization of the borates should take the following direction

a) Studies on borate chemistry should be extended, special attention being devoted to the structure of the borates and their composition in aqueous solution; and also to the study of technically important systems containing B_2O_3, and the elucidation of the underlying phenomenon of precipitation and adsorption.

b) Work on the geochemistry of boron in salt strata and on natural solutions should be considerably developed.

c) In the field of the technology of boron the conference considers the main tasks to be: the development of methods of treating low-grade raw materials and natural waters; the perfecting of existing methods of extraction and the study of new methods of extraction with ion exchange resins. The making of special ion-exchange resins for boron is regarded as promising.

5. In view of the importance of the work on boron, the Conference considers that an essential condition for the success of the work is the provision of a staff of Fellows together with the necessary space and equipment.

6. The Conference considers that its proceedings should be published.

7. It is hoped that another conference will be held in 1954.

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TO THE MEMORY OF ACADEMICIAN ILYA VASILYEVICH GREBENSHCHIKOV

The death occurred on February 8, 1953, of one of our most eminent scientists, Academician Ilya Vasilyevich Grebenshchikov, twice recipient of a Stalin prize, deputy of the Supreme Soviet of the USSR and member of the Praesidium of the USSR Academy of Sciences.

The name of Academician I. V. Grebenshchikov is associated with the development in the Soviet Union of silicon chemistry and the physical chemistry of silicates, with the organization of research institutes, and with the establishment of one of the most important branches of instrument manufacture; a first-class optical-mechanics industry. The name of Ilya Vasilyevich is well known among scientists and also to industrial workers — technologists, technicians, and operatives — within a wide circle.

I. V. Grebenshchikov was born on June 24th (12th, Old Style) 1887 in St. Petersburg into a doctor's family. In 1905 he entered the Faculty of Physics and Mathematics in the University of St. Petersburg. His inclination for scientific investigation was apparent already in his student days; before completing his university course (in 1909) he took up a post as laboratory worker in the central chemical laboratory of the Okhten gunpowder factory, where, in the course of three years he carried out several independent investigations. In 1910 Ilya Vasilyevich completed the St. Petersburg University course in brilliant fashion; he obtained a 1st Class Diploma with physical chemistry as special subject.

From 1912 to 1914 I. V. Grebenshchikov worked as an assistant to the assayer at the Mint and was assistant to the director of Laboratory for Silver and Gold Analysis. His teaching activities date from this time; he was associated with the St. Petersburg Electrotechnics Institute from 1912 to 1932, first as a teacher and later as professor of physical chemistry and theoretical electrochemistry.

The principles of physicochemical analysis developed by N. S. Kurnakov formed the basis of Ilya Vasilyevich's first investigations, and they determined his future scientific interests to a considerable degree.

While he was still working at the factory and was a student at the university, I. V. Grebenshchikov, in conjunction with N. A. Pushin, professor at the Electrotechnics Institute, began some thorough investigations on the thermal analysis of binary mixtures; these were successfully brought to a conclusion at the Electrotechnics Institute (1913). These investigations enabled the properties of eutectic points to be established, and an original pyrometric method was developed for the determination of phase transitions at high pressures; this method was used by Ilya Vasilyevich in further studies of the adiabatic compression and expansion of a number of liquids. For example, it was found that water, unlike other liquids, gave an increase in the adiabatic effect for temperatures up to 54°. I. V. associated the phenomena observed with the phase transition of ice III into ice V, and he suggested that the various modifications of water in the crystalline state correspond to various degrees of association in liquid water. Here we have a manifestation of the great intuition in scientific questions that was characteristic of Ilya Vasilyevich; in later times this intuition frequently helped him in the solution of the most complex problems.

In 1915 Ilya Vasilyevich combined his scientific activity with work directed to the solution of a problem that was of the utmost importance to Russia at that time: the organization of the production of Russian optical glass. Right from the beginning of the first World War there was an acute shortage of optical instruments, which could not be manufactured owing to the absence of optical glass. Preparations were made for the manufacture of optical glass in a Petrograd pottery (in 1915), and I. V. Grebenshchikov, then still a young research worker who had, however, already shown himself to be a talented experimenter, was invited to take direct charge of the trials on the melting of the glass. With his characteristic energy, Ilya Vasilyevich enthusiastically sat about the new task, which, thanks to his labors, has led to such great developments in the Soviet Union.

Production was soon put on its feet, and the period 1916-1917 there was an output of eight tons of glass, which, however, was still not a quality that would satisfy all the demands that were made. For a variety of reasons the works was temporarily shut down in 1920, and further investigations in this field were carried out in a newly opened research institute, in the organization of which such eminent scientists as D. S. Rozhdestvensky, I. V. Grebenshchikov, and A. I. Tudorovsky took part. Ilya Vasilyevich considered that the equipping of the laboratory with good tools and instruments was of primary importance, and with this in view he made a trip to Germany in 1922 and bought large batches of laboratory equipment; he also acquired a stock of raw materials for the production of optical glass.

Ilya Vasilyevich gathered about himself a group of young scientific workers and put into operation an enormous scheme of work on the study of the effect of the composition of glass on its properties and on the study of the nature of glass and of the process of glass formation.

Ilya Vasilyevich could not bear a bureaucratic attitude to work, and he made great demands on himself and on his subordinates. His method of direction was characteristic of him: it consisted in leaving his collaborators to their own initiative in their work, without treating them in a trivial patronizing fashion. This did not mean, however, that Ilya Vasilyevich was not indeed the director and inspirer of the researches carried out in his laboratories, guiding them and enriching them with his own ideas. There was established in this way a consolidated, purposeful group of scientific workers having their own traditions, and this served as a basis for the further development of Academician I. V. Grebenshchikov's school, from which many eminent specialists in the chemistry and technology of glass have subsequently appeared.

Ilya Vasilyevich took a direct part also in the training of personnel, not only in the Electrotechnics Institute, as mentioned above, but also in a number of other higher-education institutes, in which he gave separate lecture courses; on physical chemistry in the Polytechnical Institute (1922), in electrochemistry in the Leningrad Technological Institute (1931–1932), and on the technology of optical glass — a regular course to students of the Faculty of Physics at the university (1923–1927).

In 1923 the optical-glass works again began to operate, and Ilya Vasilyevich, as consultant, established there some extremely well-equipped laboratories, methodically directed the plans of work in the factory laboratories, and trained the personnel for them. His main work in the factory, however, was the adjustment of the technological process itself. For this purpose, the work carried out in the factory was closely coordinated with that done in the chemical laboratories directed by I. V. Grebenshchikov. Already at that time, therefore, had I. V. established a close link between science and industry.

The old method for the preparation of optical glass yielded glass of insufficiently high quality. The trouble was the so-called 'midge" – fine bubbles concentrated in the mass of glass. Ilya Vasilyevich, in conjunction with N. N. Kachalov, investigated methods for overcoming this defect.

In the summer of 1925 N. N. Kachalov, I. V. Grebenshchikov, and D. S. Rozhdestvensky decided to give up the old method and go over to a newly developed rapid method. As a result, the quality of the glass was raised considerably and the duration of the process was reduced to one-third. By 1927 the import of optical glass into the USSR had ceased completely.

During the Stalin five-year plans, when industry was confronted with the need for reconstruction and the perfection of technological processes, there arose a number of questions requiring deep study. I. V. Grebenshchikov's great scientific erudition and intuition and the boldness of his thought enabled him not only to succeed in solving the main problems of the time, but also to extend their scope far beyond the scope of the interests of glass manufacture. The investigations that he carried out acquired, in the course of their development, a fundamental scientific character, and they were of importance not only for glass chemistry, but also in the study of a number of other chemical processes.

I. V. Gribenshchikov carried out a great deal of work on heterogeneous equilibria and the physicochemical analysis of silicate systems. One of his first investigations in this field was that on the equilibrium diagram for sodium metasilicate and silica. Ilya Vasilyevich and his coworkers then studied the phase-rule diagram of the system $Na_2O-PbO-SiO_2$ which is very important for optical-glass manufacture. Several ternary compounds, which were largely dissociated in the melt, were found in this system. The authors gave a detailed characterization of the crystalline phases that separated and developed the "phase" method of investigating crystallization. Simultaneously, over a number of years, I. V. Grebenshchikov and his school carried out a detailed study of various properties of this system: viscosity, electrical conductivity, surface tension, density, optical properties, sintering temperature, thermochemical properties, chemical stability, dielectric losses; at the same time a number of new, accurate methods were developed. Extensive use was made also of X-ray methods. Later, I. V. investigated also another system: the sodium borosilicate system, which was of particular importance for various investigations carried out under his supervision. Ilya Vasilyevich and his assistants carried out a long series of investigations having the object of working out the theoretical basis of glass-forming processes: elucidation of the effect of various factors on the rate of glass formation, development of methods of preparing optically homogeneous glasses, determination of the nature of the bubbles in glass and finding methods for overcoming the defect of bubbliness, and so on.

A foremost place in the scientific investigations of I. V. Grebenshchikov is occupied by his classical studies of the surface properties of glass, which had great significance for the development of the chemistry of silicates and served as a basis for the development of a number of new technological processes.

Already in his earliest investigations the cause of the high chemical stability of silicate glasses toward water and solutions of acids was established: it is due to the protective action of a film of colloidal silicic acid 10-60 A thick formed on the surface of the glasses. On the basis of an enormous amount of experimental work, Ilya Vasilyevich later developed and supplemented these ideas, and concluded that glasses contained a silica skeleton, which formed a protective film with the silicic acid gel that was formed. The surface layer regulates the further course of the breakdown of the glass and determines a number of its properties. Under I. V. Grebenshchikov's guidance, new methods were developed for determining the thickness of the film, and of these the method based on measuring the elliptical polarization of the reflected light is worthy of note. This line of investigation turned out to be extremely fruitful, and it played a big part in establishing the mechanism of the chemical breakdown of silicates, in developing the theory of the glass electrode, and in the study and perfection of processes of grinding, polishing, and silvering glass, of methods of manufacturing optical components and of improving the light transmission of optical systems, and so on.

The ideas of Ilya Vasilyevich on the mechanism of the chemical breakdown of silicate glasses were applied also to natural silicate minerals. I. V. carried out a number of researches in this field, and they confirmed his views. His investigations on surface properties of glass stimulated a re-examination of the fundamentals of metal polishing.

Unlike foreign investigators, Ilya Vasilyevich regarded metal polishing as a process of forming and removing oxides and other compounds produced on the surface by the action of the surrounding medium. On the basis of his ideas he devised a method, new in principle, for the treatment of metal surfaces, and it proved extremely effective. The rate of making components was increased approximately fifteen times. I. V. developed new polishing agents, which have since become widely known. Under his guidance, practical handbooks on this subject were published for technologists and technicians. The chemical method of treating metal surfaces is extremely simple, and does not demand great skill; it has received wide application in industry.

I. V. Grebenshchikov, being an eminent scientist, was elected in 1932 as an active member of the USSR Academy of Sciences. As academician, Ilya Vasilyevich continued his scientific activities in the field of glass chemistry, and widened still further his associations with industry. In 1939, for the successful fulfilment of government assignments, Ilya Vasilyevich was awarded the Order of the Red Banner of Labor.

At about this time I. V. Grebenshchikov discovered a new type of glasses — the so-called microporous glasses — the investigation of which made an outstanding contribution to science, in particular to the establishment of the nature of the glass state. These glasses, which belong to the borosilicates, are characterized by their ability to retain their geometrical form, hardness, and transparency when 25% of their components are leached out with solutions of acids. Ilya Vasilyevich and his coworkers undertook a study of numerous properties of the porous glasses, and also of their micro-structure, by the aid of various chemical and physical methods. The high adsorptive power of these glasses determined their practical application. Ilya Vasilyevich attached great importance to investigations of sodium borosilicate glasses and occupied himself with such investigations up to the last days of his life.

I. V. Grebenshchikov's activities in the Academy of Sciences fell into two categories: scientific-organizational and scientific-investigational. In 1932 he was the Academician-Secretary of the Technical Group of the Division of Mathematical and Natural Sciences. In 1936, when the Division of Technical Sciences was organized, he was elected Assistant Academician-Secretary and Chairman of the Group of Technical Science and Metallurgy. In 1938 the system of the Academy of Sciences was reorganized so as to include a chemical division. Ilya Vasilyevich immediately entered the Bureau of the Division, and he took an active part in its work until his death. Owing to the illness, and later death, of Academician N. S. Kurnakov, Ilya Vasilyevich fulfilled for a time the duties of the director of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. Shortly after the election of Ilya Vasilyevich as an academician he established a small laboratory for silicate chemistry within the system of the Academy of Sciences, and this, in 1938, was merged into the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences.

A number of investigations carried out under Ilya Vasilyevich's supervision were begun in the laboratory for silicate chemistry: the development of methods for synthesizing organosilicon sompounds, investigations of the electrical conductivity of glasses, the preparation of silicates from aqueous solutions, the application of Raman spectra to the study of the structures of silicate glasses, X-ray-structure investigations on silicic acid gels, and so on. Many of these investigations continued at the Institute of Silicate Chemistry, which was established later.

In 1939 Ilya Vasilyevich switched the work of the laboratory for silicate chemistry over entirely to a study of the physicochemical properties of glazes for high-tension insulators. This work was then extremely vital. Glazes are ordinary "opal" glasses, but must have specific properties. They are essentially multicomponent low-alkali aluminosilicate systems, but at the same time are heterogeneous, since they may contain up to 15% of crystalline occlusions: the investigation of their properties, therefore, required the development of special methods. Thanks to the scientific direction of these investigations by Ilya Vasilyevich and his collaborators, the problem posed was successfully solved. By the use of the precise methods that had been developed, a small team was able to characterize those properties of the glazes that determined their behavior under the conditions of manufacture and use.

The Great Patriotic War interrupted the investigations on glazes. When war broke out, Ilya Vasilyevich switched the work of the silicate-chemistry laboratory over to work directed to the strengthening of the defenses of our Fatherland. I. V. took a great part himself in the organization of new projects and in getting going the industry that had been transferred to the East.

In 1942 Academician I. V. Grebenshchikov was awarded the Order of the Red Star, and, in the same year, was awarded a Stalin prize for scientific investigations of great importance with respect to defense. In 1943 I. V. received the very high state award: the Order of Lenin. In connection with the 220th anniversary of the founding of the USSR Academy of Sciences in 1945, Ilya Vasilyevich was awarded the Order of the Patriotic War (First Class) for outstanding services in the development of science and technology.

In the fourth Five-Year-Plan the silicate industry was presented with new problems requiring an extension of production and an improvement in the quality of building materials (glass, cement, porcelain, building ceramics, etc.) based on the development of improved technological processes and the discovery of new materials. A demand arose for the establishment of a research institute on silicon chemistry within the system of the USSR Academy of Sciences. Ilya Vasilyevich considered that a thorough study of silicon was of importance not only because its compounds are extremely wide-spread in the earth's crust and are widely employed in technology, but also because such investigations enable completely new materials to be found having valuable properties.

Immediately after the end of the war, Ilya Vasilyevich began to prepare for the establishment of the new institute. On the one hand, his preparations took the form of an extension of the activities of the silicate-chemistry laboratory, the work of which was at that time coordinated to a great extent with that of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences.

In 1946—47 the staff of the laboratory was increased and the scope of its work was widened. Ilya Vasilyevich initiated a number of investigations arising from the previous work on glazes: a study of reactions in the solid state in the $MgO-Al_2O_3-SiO_2$ system, an investigation of the interaction of natural aluminosilicate minerals with aqueous solutions, a study of the surface tension of silicate melts, etc.

On the other hand, his preparations for the establishment of the Institute took the form of a thorough consideration of its structure and lay-out. Ilya Vasilyevich arranged a number of conferences on this question in Moscow and Leningrad. Ilya Vasilyevich contemplated the establishment of a research organization, the problems of which would comprise the main general problems of the chemistry of silicon and its compounds, and also of the analogs of silicon, complex investigational methods of all kinds being employed. The sphere of the institute's activities would not be confined to silicates, although these would occupy a central place. "There is no need to fear", said Ilya Vasilyevich, "that with such an arrangement there may be a danger of a break-away from the real needs of the national economy. On the contrary, the study of all the properties of silicon as a chemical element is a prerequisite for the preparation of new materials having new properties". He accordingly planned the institute so that it would be divided into laboratories denoted, not by a branch of industry (glass, ceramics, cement, etc.), but as chemical, physicochemical, analytical, physical, etc.

The proposed structure and lay-out for the institute proposed by Academician I. V. Grebenshchikov was accepted, and by a decree of the Soviet of Ministers of December 31st, 1947 the Institute of Silicate Chemistry of the USSR Academy of Sciences was opened in Leningrad and Academician I.V. Grebenshchikov was appointed as director.

Ilya Vasilyevich considered the main problem to be the training of staff for the institute, and he devoted a great amount of attention to this matter. The institute attracted not only experienced specialists, but also many young people, with whom Ilya Vasilyevich loved to work and knew how to work. A strict and exacting director, he was at the same time a good comrade, this feature of his character being strengthened by his knowledge of and interest in people and by his sensitivity and simplicity in his intercourse with people. From the very beginning of the institute's existence he organized a scientific seminar, to which he attached great importance as a means of consolidating the team and of training the young people. The great respect and love that Ilya Vasilyevich won in the institute was expressed by the rapidity with which the whole team assimilated his high traditions.

When, in 1947, Ilya Vasilyevich attained the age of sixty, the public warmly acclaimed the occasion and the government awarded him a second Order of Lenin. His collaborators at the institute received with great joy the news of the award in 1952 of a Stalin prize to Ilya Vasilyevich.

In 1950 I. V. Grebenshchikov was elected as a deputy of the Supreme Soviet of the USSR by the workers of the Moscow electoral district of Leningrad. Ilya Vasilyevich had those basic qualities that are required of a deputy, namely a statesmanlike approach to problems, and high principles; and these, together with responsiveness, characterized his activities as a deputy. He served the people right up to his last days, examining thoroughly all the needs of constituents.

Ilya Vasilyevich Grebenshchikov lived a great and brilliant life. He fervently loved the Fatherland, and gave all his strength in its service. With the figure of Ilya Vasilyevich is associated the image of a self-effacing, but powerful personality, formed by the harmonious association within him of a great, lively, original mind and a talented, purposeful nature.

The memory of this eminent scientist, responsive, sensitive man, exacting teacher, and close friend will remain forever in the hearts of his fellow workers, his students, and all who have at any time had contact with him.

S. K. Dubrovo

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APPLICATION OF LITHIUM ALUMINUM HYDRIDE IN MICRO SYNTHESES WITH LABELED CARBON

G. I. Feklisov

In the course of investigations in which radioactive isotopes are employed, it is generally necessary first of all to prepare a pure substance having molecules that contain radioactive atoms. In some investigations in which labeled atoms are employed, it is sufficient to have a few milligrams of highly radioactive substance. Preparative chemistry has always been interested in the question of preparing compounds in micro quantities.

In the micro synthesis of compounds containing radioactive atoms, lithium aluminum hydride may be of invaluable service, owing to its valuable reducing properties. Lithium aluminum hydride is beginning to be applied widely as a reducing agent in chemical synthesis [1]. The molecule of lithium aluminum hydride contains a relatively large amount of hydrogen, thus ensuring effective reduction for a comparatively low consumption of reagent.

Most lithium aluminum hydride reduction reactions proceed with good yield at room temperature and do not give side products. By the reduction with lithium aluminum hydride of aldehydes, ketones, quinones, esters, carboxylic acids, acid anhydrides, and lactones containing radioactive elements in their molecules, the corresponding alcohols may be obtained.

If we prepare lithium hydride having radioactive hydrogen and then synthesize lithium aluminum hydride, then, using the latter as reducing agent, we may prepare a reduction product containing tritium. It is possible, of course, to use both variants simultaneously. In the present work we have used lithium aluminum hydride for the reduction of compounds containing radioactive carbon C^{14}.

EXPERIMENTAL

Preparation of lithium aluminum hydride. The synthesis of lithium aluminum hydride was carried out in bis-(2-ethoxyethyl) ether. Bis(2-ethoxyethyl) ether was prepared by the reaction:

$$ClCH_2CH_2OCH_2CH_2Cl + 2C_2H_5OH \longrightarrow C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5 + 2HCl \qquad (1)$$

$$HCl + KOH \longrightarrow H_2O + KCl. \qquad (2)$$

Caustic potash (450 g) was dissolved in 95% ethanol (900 ml) in a two-liter flask, and bis(2-chloroethyl) ether (350 g) was added to the solution obtained.

Bis(2-chloroethyl) ether may be prepared by the reaction [2]:

$$2CH_2{=}CH_2 + Cl_2O \longrightarrow ClCH_2CH_2OCH_2CH_2Cl. \qquad (3)$$

The reaction mixture – ethanol, caustic potash, and bis(2-chloroethyl) ether – was heated in the flask under reflux on a water bath for one day.

It should be noted that the reaction goes very vigorously at first, being accompanied by violent boiling of the alcohol. It was therefore necessary to have a vessel containing cold water at hand for cooling the reaction mixture when required. When reaction was complete, the solid phase was separated from liquid on a Buchner funnel having a glass filter. The filtrate was fractionally distilled, the fraction of b.p. 185-189° being collected. The bis-(2-ethoxyethyl) ether was dried for 24 hours over sodium, and again distilled, yielding 125 g (31%) of the ether, b.p. 187°, d_{15}^{15} 0.9150; n_D^{20} 1.414.

The lithium hydride used for the preparation of lithium aluminum hydride must contain not less than 80% of active product. In the present work we had commercial lithium hydride at our disposal, and before putting it into use we analyzed it for its content of active material [3], for which purpose we made use of the decomposition reaction with water:

$$LiH + H_2O \longrightarrow LiOH + H_2 \qquad (4)$$

A weighed sample of lithium hydride was introduced into a vessel of known volume connected to a manometer, and was there treated with water. The amount of hydrogen evolved as a result of reaction 4 was estimated from the increase in pressure that occurred in the vessel: by this reaction, 1 mg of lithium hydride will yield 2.8 ml of hydrogen under standard conditions of temperature and pressure. The results of the analysis of the lithium hydride for its content of active material are given in Table 1.

TABLE 1

Purity of Lithium Hydride

Expt. No.	Lithium hydride taken (mg)	Vol. of hydrogen at S.T.P. (ml)	Content of active material in lithium hydride (%)
1	72.0	183	93
2	74.8	194	93
3	62.4	157	90
4	51.0	139	95

It will be seen from Table 1 that the average content of active material in commercial lithium hydride was 93%, and it was therefore quite suitable for our purposes. The aluminum chloride taken for the synthesis was freshly sublimed.

Before performing the main synthesis, we prepared a "starter": lithium hydride powder (0.5 g) was placed in a test tube, bis(2-ethoxyethyl) ether (2 ml) was added, and a solution of aluminum chloride (0.5 g) in the same ether (3 ml) was added slowly with stirring. The preparation of lithium aluminum hydride was carried out in the apparatus represented in Fig. 1 by the reaction:

$$4LiH + AlCl_3 \xrightarrow{\text{bis(2-ethoxyethyl) ether}} LiAlH_4 + 3LiCl. \qquad (5)$$

In flask 2, lithium hydride (8.9 g; finely ground and passed through a No. 200 sieve) was placed together with the whole of the prepared "starter" with the accompanying bis(2-ethoxyethyl) ether. A solution of aluminum chloride (2.9 g) in bis(2-ethoxyethyl) ether (50 ml) was filtered through a glass filter and poured into the funnel 1. The solution of aluminum chloride was added dropwise from the funnel 1 to the lithium hydride in the flask 2 under continuous stirring. It was found desirable to allow the reaction mixture to stand for 5-6 hours after the whole of the aluminum chloride solution had been added in order to ensure that reaction was as complete as possible.

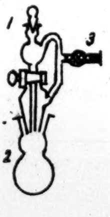

Fig. 1. Apparatus for the preparation of lithium aluminum hydride: 1) funnel for the solution of aluminum chloride in bis(2-ethoxyethyl) ether 2) reaction flask; 3) calcium chloride tube.

The solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether was separated by the aid of a glass filter from lithium chloride and unchanged lithium hydride and used for the reduction reaction. We determined the concentration of lithium aluminum hydride in the solution by treating it with water [4], the method being similar to that used for determining the purity of lithium hydride: the solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether (a few ml) was placed in a vessel of known volume, and the concentration of the solution was determined from the increase in pressure resulting from the decomposition of the lithium aluminum hydride by water according to the reaction:

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2 \qquad (6)$$

According to Equation 6, 2.4 ml of hydrogen at S.T.P. corresponds to 1 mg of lithium aluminum hydride.

Synthesis of labeled methanol. This synthesis is based on the ability of lithium aluminum hydride to reduce carbon dioxide to methanol. A radioactive preparation, $BaC^{14}O_3$, served as starting material for the preparation of labeled methanol. The procedure employed in the synthesis was first worked out with nonradioactive substances.

The preparation of methanol from carbon dioxide was carried out in a glass vacuum apparatus, which is shown diagrammatically in Fig. 2. A 0.3% solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether (50 ml) was poured into the reaction flask 2. The $BaC^{14}O_3$ preparation (0.5 g; activity 0.5 mc) was placed in flask 8 in the carbon dioxide generator, and the funnel 7, which was attached to the generator, was filled with chemically pure concentrated sulfuric acid. The apparatus was then connected to the vacuum pump and air was completely removed, first from the carbon dioxide generator and the trap, and then from the reaction vessel. Sulfuric acid was then passed dropwise from the funnel 7 to the flask 8, and radioactive carbon dioxide was obtained according to the equation:

$$BaC^{14}O_3 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + C^{14}O_2. \qquad (7)$$

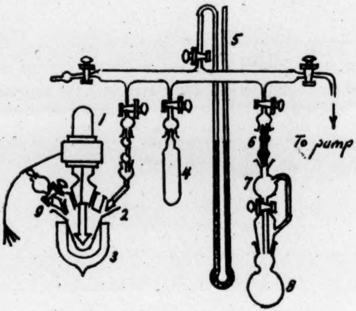

Fig. 2. Glass vacuum apparatus for the synthesis of methanol: 1) induction stirrer; 2) reaction vessel; 3) Dewar vessel for liquid nitrogen; 4) trap; 5) open mercury manometer; 6) calcium chloride tube; 7) funnel of carbon dioxide generator; 8) flask of carbon dioxide generator; 9) dropping funnel.

Carbon dioxide passed through the calcium chloride tube 6 and filled the apparatus, and when this operation was complete the induction stirrer 1 was switched on. The pressure in the system then fell appreciably owing to reaction of $C^{14}O_2$ with lithium aluminum hydride according to the equation:

$$4\overset{*}{C}O_2 + 3LiAlH_4 \longrightarrow LiAl(O\overset{*}{C}H_3)_4 + 2LiAlO_2 \qquad (8)$$

During reaction at room temperature (20°) in an apparatus of volume 500 ml, the pressure fell by 90 mm Hg. The number of moles of carbon dioxide reacting with lithium aluminum hydride can be readily calculated from Mendeleev's formula (9):

$$pv = nRT$$

$$n = \frac{pv}{RT} = \frac{90 \cdot 500}{6.2 \cdot 10^4 \cdot 293} = 0.0025 \text{ mol.} \qquad (9)$$

As a result of the reaction the $C^{14}O_2$ was completely reduced. The insignificant amount of residual radioactive carbon dioxide was transferred to the trap 4.

The method that we used for the separation of radioactive methanol depended on an exchange between the radioactive methoxyl group of the lithium–aluminum complex with the methoxyl group of inactive methanol:

$$LiAl(O\overset{*}{C}H_3)_4 + 4CH_3OH \longrightarrow LiAl(OCH_3)_4 + 4\overset{*}{C}H_3OH. \qquad (10)$$

For this purpose, methanol (50 ml) was introduced into the reaction vessel 2 from the funnel 9. The mixture was stirred with the induction stirrer 1 for six hours. When methanol is introduced into the reaction mixture, not only this exchange reaction, but also the following reaction between methanol and unchanged lithium aluminum hydride occurs:

$$LiAlH_4 + 4CH_3OH \longrightarrow LiAl(OCH_3)_4 + 4H_2. \qquad (11)$$

For this reason, it was necessary to interrupt the addition of methanol from time to time, freeze the reaction mixture with liquid nitrogen, and pump off the hydrogen that had been formed. The contents of the reaction flask were transferred to a distillation flask, and the labeled methanol was distilled from the bis(ethoxyethyl) ether. The great difference between the boiling points of these two liquids guaranteed complete removal of the methanol in a pure form. A sample of the labeled methanol was converted into $BaC^{14}O_3$, and the radioactivity of the latter was determined. The results of the radioactivity determinations are given in Table 2.

TABLE 2

Relative Radioactivity of Substances Labeled with Radiocarbon in the CH_3 Group

No.	Compound	Wt. of $BaCO_3$ (mg)	Activity of $BaCO_3$ (imp/min)	Specific activity of $BaCO_3$ $\frac{(\text{imp}\cdot\text{cm}^2)}{\text{min}\cdot\text{mg}}$	Specific activity of $BaCO_3$ per 1 C atom $\frac{\text{imp}\cdot\text{cm}^2}{\text{min}\cdot\text{mg}}$
1	$C^{14}H_3OH$	3.3	500 ± 7	204	204
		10.5	890 ± 10	198	198
2	$C^{14}H_3I$	4.1	570 ± 8	198	198
		7.4	770 ± 9	194	194
3	$C^{14}H_3CH_2OH$	5.3	330 ± 6	99	198
		9.6	480 ± 7	95	190
4	$C^{14}H_3CHO$	7.5	390 ± 7	96	192
		6.8	370 ± 6	98	196

Comparable data on the activity of radioactive samples may be obtained by calculating the specific activity: the activity of unit surface area per unit mass of the substance. When measuring the activity of C^{14} samples, changes in activity are found which depend on the thickness of the layer examined, and the latter can be found from the following considerations. If to a sample of radioactive material emitting J impulses per min. from each square centimeter of surface a layer of the material of infinitesimal thickness dx is applied, the increase in activity dJ may be written as follows:

$$dJ = a\,dx - \mu J\,dx, \tag{12}$$

where the first term of the right-hand side of the equation is associated with the formation of electrons in the disintegration of a β-active substance and is proportional to dx, and the second term is associated with the absorption of electrons in the layer dx.

In Equation 12, a is the specific activity of the sample (imp · cm²/min · mg), μ is the coefficient of self-absorption for the given substance (cm²/mg); and x is the thickness of the sample (mg/cm²).

Rearrangement of Equation 12 gives:

$$dx = \frac{dJ}{a - \mu J}, \tag{13}$$

and integration of Equation 13 gives:

$$\ln(a - \mu J)_0^J = -(\mu x)_0^x. \tag{14}$$

After performing the substitution, we have:

$$-\ln a + \ln(a - \mu J) = -\mu x \tag{15}$$

or

$$\ln\frac{a - \mu J}{a} = -\mu x. \tag{16}$$

Transformation of this gives:

$$J = \frac{a}{\mu}(1 - e^{-\mu x}). \tag{17}$$

In the limiting case when the thickness x of the layer grows indefinitely, we obtain the expression:

$$J_\infty = \frac{a}{\mu}, \tag{18}$$

and Equation 17 can therefore be written:

$$J = J_\infty(1 - e^{-\mu x}), \tag{19}$$

or

$$\frac{J}{J_\infty} = 1 - e^{-\mu x}. \tag{20}$$

By constructing the curve for the change in activity against thickness of the layer we may readily calculate the coefficient of self-absorption μ. Actually, by taking logarithms, we obtain from Equation 20:

$$\log\left(1 - \frac{J}{J_\infty}\right) = -0.434\,\mu x \tag{21}$$

which is the equation to a straight line passing through the origin. The slope of this line is clearly equal to the self-absorption coefficient μ. When this is known, the value of the specific activity may be found from the self-absorption curve and Equation 17.

Synthesis of labeled methyl iodide. For this synthesis the starting materials were labeled methanol, red phosphorus, and crystalline iodine. In carrying out the synthesis in accordance with the equation:

$$3C^{14}H_3OH + PI_3 \longrightarrow 3C^{14}H_3I + P(OH)_3 \tag{22}$$

we added finely ground crystalline iodine (48 g) in small portions to a mixture of labeled methanol (12 g) and red phosphorus (4 g) contained in a round-bottomed flask fitted with reflux condenser. After each addition of iodine, the contents of the flask were mixed by shaking and the flask was cooled with water. When the whole of the iodine had been added, the reaction mixture was shaken for 30 minutes and the flask was heated for two hours on a water bath. The methyl iodide obtained was distilled off under reduced pressure and washed in a separating funnel —

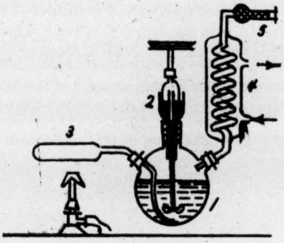

Fig. 3. Apparatus for the synthesis of ethanol labeled in the CH_3 group: 1) reaction flask; 2) stirrer with mercury seal; 3) formaldehyde generator; 4) spiral condenser; 5) calcium chloride tube.

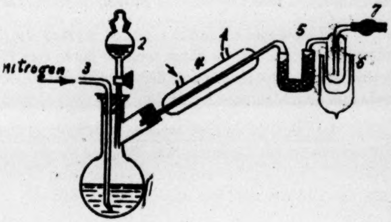

Fig. 4. Apparatus for the oxidation of ethanol: 1) reaction flask; 2) dropping funnel; 3) tube for passage of nitrogen; 4) condenser; 5) calcium chloride tube; 6) trap; 7) calcium chloride tube.

twice with water, and twice with a dilute thiosulfate solution; it was then dried, first with fused calcium chloride, and then with anhydrous sodium sulfate. The dried methyl iodide was distilled into a flask having a condenser set for downward distillation. The reaction yielded 37 g (70%) of labeled methyl iodide, b.p. 44°; its activity is given in Table 2.

Synthesis of ethanol labeled with radiocarbon in the CH_3 group. The main starting materials for this synthesis were labeled methyl iodide and paraformaldehyde. Labeled methyl iodide (30 g) was converted into methylmagnesium iodide by reaction with magnesium in diethyl ether:

$$C^{14}H_3I + Mg \longrightarrow C^{14}H_3MgI. \qquad (23)$$

The reaction was carried out in a three-necked flask fitted with dropping funnel, reflux condenser, and stirrer. The ether solution of methylmagnesium iodide that was obtained was separated from unchanged magnesium and was transferred in an atmosphere of dry nitrogen into flask 1 of the apparatus shown diagrammatically in Fig. 3. The formaldehyde generator 3 was charged with paraformaldehyde that had been dried over phosphoric oxide for one month, the quantity being sufficient to ensure a 75% excess over that theoretically required. The formaldehyde obtained by pyrolytic decomposition of the paraformaldehyde was passed into the ether solution of methylmagnesium iodide, when a complex was formed in accordance with the reaction:

$$C^{14}H_3MgI + HCHO \longrightarrow C^{14}H_3CH_2OMgI. \qquad (24)$$

In carrying out this reaction, the ether was maintained at an even gentle boil by regulation of the velocity of the formaldehyde stream; the ether must not be allowed to boil violently.

The complex formed in accordance with Equation 24 gives ethanol when decomposed with water:

$$C^{14}H_3CH_2OMgI + H_2O \longrightarrow C^{14}H_3CH_2OH + MgI(OH). \qquad (25)$$

The reaction of Equation 24 has not yet been described in the literature [5]. The ethanol obtained was distilled from the reaction mixture. After being dried over anhydrous sodium sulfate and distilled several times it had b.p. 78°, n_D^{20} 1.365, and the activity given in Table 2. The yield of labeled ethanol was 7 g (70%).

Preparation of labeled acetaldehyde from ethanol. Labeled acetaldehyde was prepared by the oxidation of ethanol with chromic acid in the apparatus shown in Fig. 4. A solution of Na_2CrO_4 (10 g) in 30% sulfuric acid (20 ml) was added dropwise from dropping funnel 2 into a boiling mixture of $C^{14}H_3CH_2OH$ (6 g) in 40% sulfuric acid (7 ml) contained in flask 1. At the same time a stream of nitrogen passed by the tube 3 through the reaction mixture and carried away the acetaldehyde formed. This passed through the condenser 4 and the U-tube containing calcium chloride (5), and was so freed from water and alcohol. The acetaldehyde was frozen out in the trap 6, which was surrounded by liquid nitrogen contained in a Dewar vessel. The acetaldehyde was purified by repeated distillation under reduced pressure followed by distillation on a water bath at atmospheric pressure; it then boiled at 20°.

The alcohol oxidation reaction yielded 4 g (70%) of labeled acetaldehyde. As a check on the chemical purity of the product, its vapor pressure curve (see Fig. 7) and its activity (Table 2) were determined. Also, in verification of the location of the labeled carbon in the molecule, we carried out a degradation of the acetaldehyde, for which purpose we made use of the iodoform reaction. These experiments are described below.

Synthesis of ethanol labeled with radiocarbon in the 1 position. The synthesis of ethanol labeled with radiocarbon in the 1-position was effected by the reduction of labeled ethyl acetate with lithium aluminum hydride. As we had a radioactive preparation of $BaC^{14}O_3$ at our disposal, we prepared radioactive barium acetate from it. The synthesis was carried out as follows:

$$BaC^{14}O_3 \xrightarrow{H_2SO_4} C^{14}O_2. \qquad (26)$$

$$CH_3MgI \xrightarrow{C^{14}O_2} CH_3C^{14}OOMgI \xrightarrow[Ba(OH)_2]{H_2O} (CH_3C^{14}OO)_2Ba \qquad (27)$$

The synthesis of acetic acid labeled in the carboxyl group was carried out in the way already described [6,7]: by carboxylation of inactive methylmagnesium iodide with radioactive carbon dioxide obtained by decomposition of the $BaC^{14}O_3$ preparation with concentrated sulfuric acid. When carbon dioxide was passed into an ether solution of methylmagnesium iodide, a complex was obtained, which gave acetic acid on being decomposed with water. The acid obtained was purified and then converted into the barium salt by titration with barium hydroxide solution.

In the micro synthesis of ethyl acetate, barium acetate (0.5 g) having an activity of 0.4 mc was placed in the reaction flask 2 of the apparatus shown in Fig. 5. Concentrated sulfuric acid (0.7 g) was added, and the mixture was heated on an oil bath to 140°; ethanol (3 ml) was added dropwise from the funnel 1. In order to effect the return of the ethanol and acetic acid vapors to the reaction vessel, the flask 2 was provided with a reflux condenser 3, cooled with air that had passed through liquid nitrogen in the Dewar vessel 4. The active ethyl acetate obtained as a result of the reaction:

$$(CH_3C^{14}OO)_2Ba + C_2H_5OH \xrightarrow{H_2SO_4} CH_3C^{14}OOC_2H_5. \qquad (28)$$

was collected in the trap 5, which was cooled with liquid nitrogen. The ethyl acetate was purified from alcohol by washing in a separating funnel with aqueous calcium chloride solution, and it was then fractionally distilled.

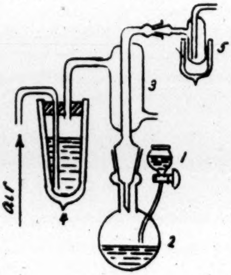

Fig. 5. Apparatus for the micro synthesis of ethyl acetate: 1) dropping funnel; 2) reaction flask; 3) condenser; 4) Dewar vessel; 5) trap.

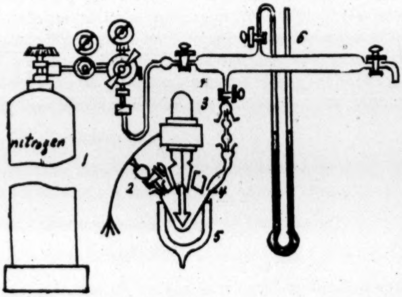

Fig. 6. Diagram of glass apparatus for the synthesis of ethanol labeled with radiocarbon in the 1-position: 1) nitrogen cylinder; 2) dropping funnel; 3) induction stirrer; 4) reaction vessel; 5) Dewar vessel; 6) open mercury manometer.

The yield of active ethyl acetate was 0.3 g (90%). The reduction of the ethyl acetate to ethanol with lithium aluminum hydride was carried out in a glass apparatus, which is shown diagrammatically in Fig. 6.

Before the reaction was carried out, the air was blown out of the apparatus with dry nitrogen from the cylinder 1.

A 0.5% solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether (50 ml) was poured into the reaction vessel 4, and ethyl acetate (0.3 g of radioactive, and 0.3 g of inactive) was added. The apparatus was then closed, and the reduction proceeded under constant stirring (induction stirrer 3).

The first stage of the reduction of ethyl acetate to ethanol by the aid of lithium aluminum hydride consists in the formation of a lithium–aluminum complex:

$$2\mathrm{CH_3\overset{\bullet}{C}OOC_2H_5} + \mathrm{LiAlH_4} \longrightarrow \mathrm{LiAl(CH_3\overset{\bullet}{C}H_2O)_4}. \tag{29}$$

When reaction was complete, the production of radioactive ethanol was effected, as in the case of the methanol synthesis, by the exchange of the radioactive ethoxyl group of the lithium–aluminum complex with that of inactive ethanol:

$$\mathrm{LiAl(CH_3\overset{\bullet}{C}H_2O)_4} + \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{LiAl(CH_3CH_2O)_4} + \mathrm{CH_3\overset{\bullet}{C}H_2OH}. \tag{30}$$

For this purpose, inactive ethanol (20 ml) was added to the reaction mixture from the funnel 2. It was necessary to interrupt the reaction from time to time by freezing the reaction mixture with liquid nitrogen so that hydrogen formed by the reaction of Equation 11 could be removed.

The mixture, which consisted essentially of bis(2-ethoxyethyl) ether and ethanol, was transferred to a distillation flask, and the labeled ethanol was distilled off. A sample of the ethanol labeled with radiocarbon in the 1-position was converted into $BaCO_3$, the radioactivity of which is given in Table 3.

TABLE 3

Relative Radioactivity of Ethanol and Acetaldehyde

No.	Compound	Wt. of $BaCO_3$ (mg)	Activity of $BaCO_3$ (imp/min)	Specific activity of $BaCO_3$ $\frac{\mathrm{imp \cdot cm^2}}{\mathrm{min \cdot mg}}$
1	$CH_3C^{14}H_2OH$	11.8	490 ± 7	102
		6.9	410 ± 7	105
2	$CH_3C^{14}HO$	6.2	380 ± 6	102
		4.2	280 ± 6	99

From the alcohol obtained, acetaldehyde labeled with radiocarbon in the carbonyl group was prepared by the method given above. The acetaldehyde was converted into $BaCO_3$, which showed the relative radioactivity given in Table 3. As in the preparation of acetaldehyde labeled in the CH_3 group, we again determined the vapor pressure of the product. The results obtained are shown in Fig. 7, in which the crosses correspond to the results for acetaldehyde labeled in the carbonyl group, and the circles to results for acetaldehyde labeled in the CH_3 group. The vapor pressure curves for our products coincided within the limits of experimental error with the curve constructed from data in the literature [8], thus indicating that the acetaldehyde samples were of high purity.

In order to check the position of the labeled carbon in the molecule, we carried out the degradation of samples of acetaldehyde by the aid of the reaction with KOI, which proceeds according to the equation:

$$\mathrm{CH_3\overset{\bullet}{C}HO} + 3\mathrm{KOI} \longrightarrow \mathrm{CHI_3} + \mathrm{H\overset{\bullet}{C}OOK} + 2\mathrm{KOH}. \tag{31}$$

Results of activity determinations on iodoform and potassium formate are given in Table 4.

TABLE 4

Relative Radioactivity of the Products of the Degradation of Acetaldehyde Isomers

No.	Acetaldehyde and its degradation products	Chemical composition of samples for counting	Wt. of sample (mg)	Activity of sample (imp/min)	Specific activity $\frac{\mathrm{imp \cdot cm^2}}{\mathrm{min \cdot mg}}$	Specific activity per 1 C atom $\frac{\mathrm{imp \cdot cm^2}}{\mathrm{min \cdot mg}}$
1	$CH_3C^{14}HO$	$BaCO_3$	6.2	380 ± 6	102	204
			4.2	280 ± 6	99	198
	CHI_3	CHI_3	11.2	1 ± 2	0	0
			5.6	0 ± 2	0	0
	HCOOH	HCOOK	10.0	780 ± 9	179	179
			6.3	700 ± 8	185	185
2	$C^{14}H_3CHO$	$BaCO_3$	3.4	26 ± 2	10	20
			4.6	31 ± 2	10	20
	CHI_3	CHI_3	3.8	48 ± 2	18	18
			4.3	50 ± 2	17	17
	HCOOH	HCOOK	10.8	2 ± 2	0	0
			5.1	0 ± 2	0	0

Examination of the results given in Table 4 will show that one of the samples of acetaldehyde did indeed contain labeled carbon in the 1-position only, whereas the other contained it only in the 2-position. This proves the correctness of our procedure in these syntheses.

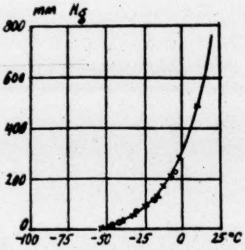

Fig. 7. Vapor pressure curve for acetaldehyde: xxx acetaldehyde labeled in the carbonyl group; ooo acetaldehyde labeled in the CH_3 group.

SUMMARY

1. Lithium aluminum hydride has been prepared in bis-(2-ethoxyethyl) ether.

2. A method has been devised for the micro synthesis and isolation of methanol labeled with radiocarbon.

3. Ethanol labeled with radiocarbon in the CH_3 group has been synthesized for the first time.

4. A method has been devised for the micro synthesis of labeled ethyl acetate from barium acetate.

5. A method has been devised for the micro synthesis and isolation of ethanol labeled with radiocarbon in the 1-position.

6. Two isotopic isomers of acetaldehyde have been prepared.

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REACTIONS OF VITREOUS SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 1. REACTIONS OF VITREOUS SODIUM SILICATES WITH WATER AND WITH HYDROCHLORIC ACID SOLUTIONS

S. K. Dubrovo and Yu. A. Shmidt

According to modern views, bonds of two types are present in vitreous sodium silicates: the silicon—oxygen bond, which is very nearly homopolar in character, and the electrostatic bond between sodium ions and oxygen.

When water or solutions of acids act on sodium silicate glasses, the primary result is the rupture of the O—Na bond. Sodium ions, being very mobile, are readily replaced by hydrogen ions present in the solution [1], and the exchange reaction that occurs may be represented as follows:

$$Na^+ (glass)^- + H^+ \rightleftarrows H^+ (glass)^- + Na^+ \qquad (1)$$

When water acts on sodium silicate glasses, OH^- ions are formed simultaneously in equivalent amount, and the process may be represented as surface hydrolysis of sodium silicate accompanied by passage of alkali into solution. As a result of the exchange reaction between sodium ions and hydrogen ions, silicic acid is formed at the surface of the glass. According to Grebenshchikov's views [2], this silicic acid, together with the original silica of the glass (which forms a three-dimensional skeleton of silicon—oxygen tetrahedra), constitutes a protective layer that preserves the glass from further breakdown. The thickness and structure of the protective surface layer largely determine both the rate of diffusion of sodium ions from the unattacked glass and the movement of hydrogen ions in the opposite direction. When water acts on sodium silicates the alkaline solution formed as a result of the exchange reaction may in its turn attack the protective surface layer by bringing the silicic acid into solution, i.e. a secondary reaction may ensue. The strength of the protective layer evidently depends on the number of silicon—oxygen tetrahedra directly linked together, and this number characterizes the degree of polymerization of silica in the original glass.

If the amount of SiO_2 going from the sodium silicate to the solution is less than the amount of Na_2O transferred, then we have leaching of alkali from the glass: this occurs in the case of glasses of relatively high silica content. In the opposite case, we have what may be termed "dissolution" of the glass. All factors encouraging depolymerization of silica in vitreous sodium silicates will facilitate transfer of SiO_2 into solution and so increase the breakdown of these glasses. It is therefore necessary, when characterizing the chemical stability of sodium silicate glasses, that rupture of bonds of both types should be taken into consideration.

Study of the interaction of vitreous sodium silicates with aqueous solutions is of great interest, for the investigation of a system of such simple character enables the relation between the composition of glass and its susceptibility to attack by chemical agencies to be established more exactly. Such a study may serve as a basis for the study of the complex systems found in technical silicate materials. It would be of interest also to settle the disputed question, whether the susceptibility of vitreous sodium silicates to attack can be related to the phase diagram of the system.

There are very few data in the literature on the chemical stability of the Na_2O-SiO_2 system. Turner and his coworkers [3] investigated only three sodium silicates ($Na_2O \cdot 2SiO_2$, $Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 4SiO_2$) with respect to the effect of various reagents. They determined the loss in weight of the silicate in powder form when boiled (10 g samples) for one hour, and they found the loss fell rapidly as the SiO_2 content of the original glass was raised.

We have undertaken an investigation of the interaction of a number of vitreous sodium silicates and aluminosilicates with aqueous solutions. We considered it desirable to determine the susceptibilities of these silicates to attack by determining the amounts of the components going into solution as a function of the time. The present paper gives the results of an investigation into the action of water and hydrochloric acid solutions on vitreous sodium silicates having compositions corresponding to the invariant points on the phase diagram of the system Na_2O-SiO_2, to intermediate points, and also to points representing high silica contents (Fig. 1).

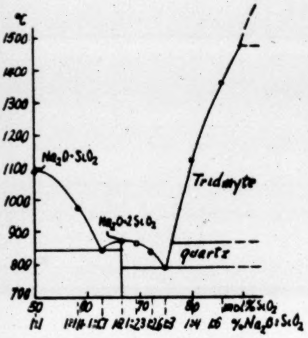

Fig. 1. Phase diagram of the system Na_2O-SiO_2 (the positions of the silicates investigated are indicated by circles)

TABLE 1

Composition of Sodium Silicate Melts

Molecular ratio	Composition by synthesis				Composition by analysis (wt.%)		Annealing temp.
	Mol.%		Wt. %.				
$Na_2O:SiO_2$	Na_2O	SiO_2	Na_2O	SiO_2	Na_2O	SiO_2	(°C)
1:1 *	50.0	50.0	50.8	49.2	—	—	420
1:1.4	41.7	58.3	42.5	57.5	42.2***	57.8	440
1:1.7**	37.1	62.9	37.9	62.1	37.8	62.1	460
1:2*	33.3	66.7	34.1	65.9	33.8	65.8	480
1:2.3	30.3	69.7	31.0	69.0	31.0	69.0	490
1:2.6	27.8	72.2	28.5	71.5	28.6	71.6	495
1:3**	25.0	75.0	25.6	74.4	25.6	74.2	500
1:4	20.0	80.0	20.5	79.5	20.5	79.3	510
1:6	14.3	85.7	14.7	85.3	15.0***	85.0	540

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* Correspond to sodium metasilicate and disilicate on the phase diagram.

** Correspond to eutectics on the phase diagram.

*** By difference.

EXPERIMENTAL

Preparation of Sodium Silicate Glasses

Our starting materials for the preparation of sodium silicate glasses were sodium carbonate (analytically pure) and crushed quartz containing not more than 0.2% of impurities. The glasses were prepared in a platinum crucible, under mechanical stirring by means of a platinum stirrer, at a temperature of 1200-1400° (depending on the composition) in a furnace provided with Silit resistors. The molten glass was poured into iron molds, being pressed into each mold with an iron rod. The resulting samples were in the form of discs having a surface of 10-12 sq.cm and an almost perfect cylindrical shape. The samples were immediately annealed carefully in the muffle. The quality of the annealing treatment was checked by the aid of a polariscope. The annealed samples were preserved in a desiccator over sulfuric acid. In order to check the reproducibility of results, duplicate preparations were made for some of the sodium silicates. The compositions of the glasses prepared (as determined by synthesis and analysis) are given in Table 1.

Procedure

The experiments were carried out at 25° and 40° in an air thermostat having a bimetal thermoregulator; the temperature variation was within ±0.5°. In the water experiments, the beakers and their covers, the stands for the samples, and the stirrers were all of silver; in the hydrochloric acid experiments, quartz apparatus was used. The liquid was first heated to the required temperature, and the sample, previously measured up with calipers, was then placed in the beaker. The stirrer (300 r.p.m.) was switched on, and samples of the liquid were taken at definite intervals of time and were analyzed for sodium and SiO_2. In the experiments with high-silica silicates, containing 75 mol.-% of SiO_2 and more, the amounts of the components passing into the solution were so small that it was necessary to take large amounts of liquid for analysis, and one experiment was not sufficient for the obtaining of the necessary number of points. It was therefore necessary to perform a number of experiments with some samples, times of 1.4 and 12 hours being employed and a selection of intermediate points being taken.

In the case of some of the sodium silicates, the action of water was determined at 100°, the glasses being boiled in a silver beaker for one hour and the liquid then analyzed. In the water experiments, the amount of sodium going into the solution was determined from the alkalinity of the solution as found by titration with 0.01 N HCl (Neutral Red indicator); in the acid experiments, it was determined by a colorimetric method developed for glass analysis by Krupkin [4]. The silicic acid in the solution was determined colorimetrically, the yellow complex formed with ammonium molybdate being used for this purpose. In this investigation we have employed a variant of this method, developed by one of us [5], which permits separate determination in the solution of molecularly dispersed and polymerized silicic acid. In the latter case a preliminary treatment with alkaline solutions is given. When it was found necessary, a more sensitive method of silicic acid determination was used: the method proposed by Usatenko and Orlova [6], in which the silicomolybdate complex is reduced with Mohr's salt to molybdenum blue. The amounts of alkali and silicic acid found in the solution were then recalculated as moles of the corresponding oxides (Na_2O and SiO_2) going into solution from 1 sq.cm of surface (denoted by n_{Na_2O} and n_{SiO_2}). This method of expressing the analytical results makes it easy to compare the amounts of the components going into solution with their contents in the original glass, and it facilitates the interpretation of the results obtained.

In order to characterize the process of interaction we employed also several other quantities. If the composition of the glass is expressed in the form $Na_2O \cdot mSiO_2$, then the amount of SiO_2 in the layer of glass that has undergone reaction will be $m \cdot n_{Na_2O}$, and the fraction of this (α) which has passed from this layer to the solution will be $\frac{n_{SiO_2}}{m \cdot n_{Na_2O}}$. Thus α is the fraction of the silicic acid that has passed into the solution from the layer of glass that has undergone reaction, and its value permits us to form an idea of the nature of the process that is taking place. When $\alpha = 1$, the components are passing into the solution in the same proportions as those in which they occur in the glass, i.e. dissolution is occurring. On the other hand, when $\alpha = 0$, leaching is occurring, with the result that a layer of silicic acid remains on the surface of the glass. Furthermore, knowing the amount of Na_2O that has passed into solution, we may, with certain assumptions, calculate the depth of the disrupted layer of glass, the required formula being:

$$\delta_{Na_2O} = \frac{n_{Na_2O} \cdot M \cdot 100}{ad}, \qquad (2)$$

TABLE 2

Interaction of Vitreous Sodium Silicates with Water at 25°

Molar ratio $Na_2O:SiO_2$	Coefficients	Time										
		minutes					hours					
		2.5	5	10	15	30	1	2	4	6	8	12
1:1	$n_{Na_2O} \cdot 10^6$	246	590	1250	—*	—**	8000***	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	245	590	1260	—	—	8000***	—	—	—	—	—
	α	1.00	1.00	1.01	—	—	1.0	—	—	—	—	—
1:1.4	$n_{Na_2O} \cdot 10^6$	4.1	7.5	13	19	35	79	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	2.6	4.4	8.4	14	35	101	—	—	—	—	—
	α	0.45	0.42	0.46	0.53	0.71	0.91	—	—	—	—	—
1:1.7	$n_{Na_2O} \cdot 10^6$				6.0	10	17	28	45	61	—	—
	$n_{SiO_2} \cdot 10^6$				1.8	2.2	3.4	5.3	12	18	—	—
	α				0.18	0.13	0.12	0.11	0.16	0.17	—	—
1:2	$n_{NaO_2} \cdot 10^6$					4.6	7.6	13	20	26	32	43
	$n_{SiO_2} \cdot 10^6$					0.2	0.6	1.2	2.1	2.6	3.0	3.5
	α					0.02	0.04	0.05	0.05	0.05	0.05	0.04

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* It was now no longer possible to take the surface area as having its initial value.

** The sample dissolved completely.

*** Extrapolation.

where n_{Na_2O} is the amount of Na_2O going into the solution (moles/sq.cm); $\underline{M}$ is the molecular weight of Na_2O; $\underline{a}$ is the amount of Na_2O in the glass (wt. %); $\underline{d}$ is the density of the glass.

The value of δ_{SiO_2}, expressing the reduction in the thickness of the silicic acid layer due to its dissolution, may be calculated in a similar manner. The difference in these quantities, $\delta = \delta_{NaO_2} - \delta_{SiO_2}$, gives the thickness of the silicic acid layer on the surface of the glass. This calculation, of course, is of a conditional nature, for it is

TABLE 3

Interaction of Vitreous Sodium Silicates with Water at 40°

Molar ratio $\frac{Na_2O}{SiO_2}$	Coefficients	Time											
		Minutes						Hours					
		2.5	5	7.5	10	15	30	1	2	4	6	8	12
$\frac{1}{1}$	$n_{Na_2O} \cdot 10^6$	458	1030	1470	—*	—	—**	12000***	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	450	1040	1500	—	—	—	12000***	—	—	—	—	—
	a	1.0	1.0	1.0	—	—	—	1.0	—	—	—	—	—
$\frac{1}{1.4}$	$n_{Na_2O} \cdot 10^6$	15	34	—	72	108	218	439	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	18	46	—	100	152	304	605	—	—	—	—	—
	a	0.86	0.97	—	0.99	1.00	1.00	1.0	—	—	—	—	—
$\frac{1}{1.7}$	$n_{Na_2O} \cdot 10^6$	3.6	6.4	—	8.2	14	28	51	104	220	342	—	—
	$n_{SiO_2} \cdot 10^6$	1.6	2.8	—	4.6	7.2	15	33	140	350	566	—	—
	a	0.26	0.26	—	0.33	0.30	0.31	0.38	0.79	0.94	0.97	—	—
$\frac{1}{2}$	$n_{Na_2O} \cdot 10^6$	1.7	2.8	—	4.9	6.6	11	18	30	47	62	76	101
	$n_{SiO_2} \cdot 10^6$	0.07	0.25	—	0.66	1.2	2.3	3.2	4.2	5.8	9.3	13	26
	a	0.02	0.04	—	0.07	0.09	0.10	0.09	0.07	0.06	0.08	0.09	0.13
$\frac{1}{2.3}$	$n_{Na_2O} \cdot 10^6$						5.1	9.1	15	25	32	38	51
	$n_{SiO_2} \cdot 10^6$						0.12	0.24	0.54	0.83	1.0	1.3	2.1
	a						0.010	0.011	0.014	0.015	0.014	0.015	0.018
$\frac{1}{3}$	$n_{Na_2O} \cdot 10^6$							1.6	2.5	3.6	4.7	5.5	7.2
	$n_{SiO_2} \cdot 10^6$							0.040	0.046	0.065	0.078	0.092	0.11
	a							0.008	0.006	0.006	0.006	0.006	0.005
$\frac{1}{4}$	$n_{Na_2O} \cdot 10^6$							0.75	0.93	1.2	1.4	1.6	2.0
	$n_{SiO_2} \cdot 10^6$							0.016	0.017	0.022	0.030	0.038	0.040
	a							0.005	0.005	0.005	0.005	0.006	0.005
$\frac{1}{6}$	$n_{Na_2O} \cdot 10^6$							0.30	0.38	0.48	0.55	0.61	0.69
	$n_{SiO_2} \cdot 10^6$							0.009	—	0.012	0.011	0.012	0.013
	a							0.005	—	0.004	0.003	0.003	0.003

---

* It was now no longer possible to take the surface area as having its initial value.

** The sample dissolved completely.

*** Extrapolation.

made on the supposition that the residual film consists only of silicic acid and does not contain Na_2O, and that the boundaries between unchanged glass and film and between film and solution are parallel to the original surface of the glass, the dissolution of silicic acid occurring only from the surface of the film. Also, this calculation takes no account of the change in the volume of the film, as compared with the volume of the original glass. Nevertheless, in spite of the conditional nature of the calculations, the results obtained permit a very graphic comparison of the various sodium silicates. Thus, by the aid of the method described above it has been possible to characterize the course of the breakdown process in sodium silicates.

Interaction of Sodium Silicates with Water

The experiments were carried out on eight sodium silicates. The results relating to the interaction of these silicates with water at 25°, 40°, and 100° are given in Tables 2, 3, and 4, and also in Fig. 2. The duration of the experiment varied from ten minutes to twelve hours, depending on the composition of the silicate.

TABLE 4

Interaction of Vitreous Sodium Silicates with Water*

Coefficients	$Na_2O : SiO_2$				
	1:2	1:2.3	1:3	1:4	1:6
$n_{Na_2O} \cdot 10^6$	3200	990	69	5.8	1.4
$n_{SiO_2} \cdot 10^6$	6400	2200	102	1.4	0.12
α	1.0	0.97	0.49	0.060	0.014

It will be seen from the results given in Tables 2 and 3 that in the case of the interaction of sodium metasilicate with water at 25° and 40° the components of the glass go into solution in the same ratio as that in which they are found in the glass; dissolution is therefore occurring ($\alpha = 1$). Dissolution is very rapid: a 2-g sample dissolved completely in 15-20 minutes, yielding a clear solution.

As the silica content of the sodium silicates increases, there is a considerable reduction in the absolute amounts of the components going into solution, and the transfer of SiO_2 lags behind that of Na_2O. Consequently, the value of α diminishes, which is evidence of the presence of a residual layer of silica on the surface of the glass. For the silicate of composition $Na_2O \cdot 1.4SiO_2$, however (and to some extent also for $Na_2O \cdot 1.7SiO_2$ at 40°), an appreciable lag in the transfer of SiO_2 can be observed only in the early stages; the value of α then becomes equal to, or nearly equal to, unity. This may be explained, on the one hand, by the increase in the alkalinity of the solution with time due to the entry of Na_2O from the glass: this leads to dissolution of the surface layer of silicic acid that has formed, and so to a reduction in its thickness. On the other hand, the thinning of the silicic acid layer facilitates the passage of Na_2O into the solution, and so itself contributes to the thickening of the layer. As a result, an equilibrium is established in which the thickness of the film increases, because of the passage of Na_2O into solution, to almost the same extent as it diminishes because of dissolution of silicic acid from the surface. Dissolution of the glass appears to occur, and it proceeds in such a way that there is always a layer of silicic acid on the surface; as a result, the value of α approaches unity only asymptotically.

Experiments with sodium disilicate at 25° and 40° showed that α has values of 0.02-0.13. The silicic acid film is now stronger, and its restraining action on the transfer of Na_2O into solution is quite marked. In the case of silicates of higher silica content, only an insiginificant amount of the silicic acid passes into solution at 40° (α = 0.02-0.003); the bulk of it remains on the surface. When the temperature is raised to 100°, the amounts of the components (particularly SiO_2) going into solution increase considerably (see Table 4); as a result the value of α increases, indicating, in the case of the less stable silicates, e.g. $Na_2O \cdot 2SiO_2$, a transition from leaching to dissolution.

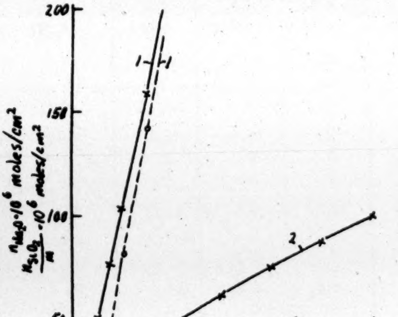

Fig. 2. Interaction of vitreous sodium silicates with water at 40°: 1 - $Na_2O \cdot 1.7 SiO_2$; 2 - $Na_2O \cdot 2SiO_2$; 3 - $Na_2O \cdot 2.3SiO_2$; 4 - $Na_2O \cdot 3SiO_2$; 5 - $Na_2O \cdot 4SiO_2$; x—x—n_{Na_2O} o—o—$\frac{n_{SiO_2}}{m}$

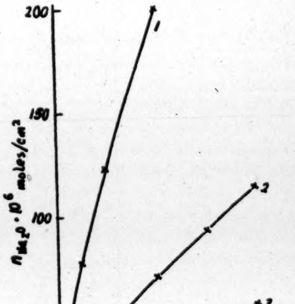

Fig. 3. Interaction of vitreous sodium silicates with 0.1 N hydrochloric acid: 1) $Na_2O \cdot 1.7 SiO_2$; 2) $Na_2O \cdot 2SiO_2$; 3) $Na_2O \cdot 2.3 SiO_2$; 4) $Na_2O \cdot 2.6 SiO_2$; 5) $Na_2O \cdot 3SiO_2$; 6) $Na_2O \cdot 4SiO_2$

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* Experiments were at 100° for one hour.

It was established that when sodium silicates interact with water the whole of the silicic acid going into solution is in a molecularly dispersed state and may be determined, without preparatory treatment, by the colorimetric method.

Interaction of Sodium Silicates with Hydrochloric Acid Solutions

A study was made of the interaction of six sodium silicates with 0.1 N hydrochloric acid at 40°. In order to determine the effect of the concentration of acid on the susceptibilities of sodium silicates to attack, an investigation was made of the action of 0.01 N, 0.1 N, and N solutions of hydrochloric acid on a sodium silicate of molecular composition $Na_2O \cdot 2.6 SiO_2$. The experiments were of eight hours' duration, and tests were made after 1, 2, 4, 6, and 8 hours. The results on the action of acids on the investigated sodium silicates are given in Table 5 and in Fig. 3. As will be seen from these results, the extent to which Na_2O passes into the solution falls rapidly as the SiO_2 content of the original silicate increases, as in the case of the experiments with water. The absolute values of the amounts of Na_2O passing into solution are higher for the acid solutions than for water Beginning with the silicate of composition $Na_2O \cdot 4SiO_2$, the amount of Na_2O passing into solution becomes very small (not more than $2 \cdot 10^6$ moles/sq. cm in eight hours, both in the case of water and of acids). The action of acids is characterized by a more marked lag of silicic acid behind Na_2O in its passage into the solution. Even with such an unstable silicate as $Na_2O \cdot 1.7SiO_2$, an appreciable layer of silicic acid remains on the surface after a four hours' treatment with acid (a = 0.227), whereas for treatment with water under these conditions a approaches unity and this silicate practically dissolves.

TABLE 5

Interaction of Vitreous Sodium Silicates with Hydrochloric Acid Solutions at 40°

Molar ratio $Na_2O:SiO_2$	Normality of acid	Coefficients	Time (hours)					
			0.5	1	2	4	6	8
1:1.7	0.1	$n_{Na_2O} \cdot 10^6$	51.6	78.1	122.6	200.6	–	–
		$n_{SiO_2} \cdot 10^6$	0.3	0.7	5.4	77.8	–	–
		a	0.003	0.005	0.026	0.227	–	–
1:2.0	0.1	$n_{Na_2O} \cdot 10^6$		29.9	46.5	71.1	94.2	108.9
		$n_{SiO_2} \cdot 10^6$		0.02	0.03	0.1	0.2	0.3
		a		0.0003	0.0003	0.0007	0.001	0.001
1:2.3	0.1	$n_{Na_2O} \cdot 10^6$	–	14.9	22.4	35.3	48.4	57.2
		$n_{SiO_2} \cdot 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:2.6	0.01	$n_{Na_2O} \cdot 10^6$	–	5.6	9.6	16.8	22.3	26.5
		$n_{SiO_2} \cdot 10^6$	–		0	0	0	0
		a	–	0	0	0	0	0
1:2.6	0.1	$n_{Na_2O} \cdot 10^6$	–	6.0	10.2	18.5	22.8	28.2
		$n_{SiO_2} \cdot 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:2.6	1	$n_{Na_2O} \cdot 10^6$	–	4.5	8.3	16.2	20.9	25.4
		$n_{SiO_2} \cdot 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:3.0	0.1	$n_{Na_2O} \cdot 10^6$	–	2.7	4.3	5.7	8.1	10.0
		$n_{SiO_2} \cdot 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:4.0	0.1	$n_{Na_2O} \cdot 10^6$	–	0.7	1.0	1.2	1.5	1.7
		$n_{SiO_2} \cdot 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0

When the silicate $Na_2O \cdot 2.3 SiO_2$ and silicates of higher silica content were treated with hydrochloric acid solutions, no silicic acid could be detected in the solution. On the other hand, in the water experiments silicic acid was found in the solution even in the case of the silicate $Na_2O \cdot 6SiO_2$.

As will be seen from Table 5, variation in hydrochloric acid concentration from 0.01 N to N has practically no effect on the amount of Na_2O passing into solution from the silicate of composition $Na_2O \cdot 2.6 SiO_2$.

DISCUSSION OF RESULTS

The way in which the amounts of the components passing into solution depend on the silica contents of the sodium silicates submitted to the action of water and of hydrochloric acid solutions is shown in Figures 4 and 5. In the case of water, these figures show that the relationship is expressed by a number of similar smooth curves.

For the action of hydrochloric acid solutions at 40°, the relationship between the logarithm of the amount of Na_2O passing into solution and the molecular proportion of SiO_2 in the glass is almost a linear one (Fig. 5). Both for water and for acids there are no perceptible deviations at compositions corresponding to the invariant points of the Na_2O-SiO_2 phase diagram. It will be seen from the results presented that increase in silica content has a particularly marked effect in reducing the tendency for leaching to occur from sodium silicate glasses when the latter are based on silicates of low stability; further increase in silica content does not have such a powerful effect. Features described by other investigators who have studied the stability of sodium and potassium silicate glasses [7] — a linear logarithmic relation between the amount of alkali passing into solution and the molecular proportion of SiO_2 in the glass, and deviations at the points corresponding to disilicate — have not been confirmed in our experiments.

The interaction of vitreous sodium silicates with aqueous solutions is extremely complex and depends on a number of factors. The main factors determining the rate of the breakdown of sodium silicates are: the state of the silica in the original glass, the hydrogen ion concentration in the solution, and the thickness and structure of the protective surface film. The latter is, of course, largely determined by the state of silica in the original glass.

As will be seen from the results presented, the main process occurring in sodium silicates having a relatively high silica content (and therefore a relatively high number of directly united silicon-oxygen tetrahedra) is the leaching out of sodium oxide by water. The alkaline solution formed as a result of the exchange of sodium ions for hydrogen ions is not able to disrupt the robust skeleton to an appreciable extent: evidence for this is to be found in the low concentration of SiO_2 in the solution.

In the case of silicates such as $Na_2O \cdot 1.4SiO_2$, $Na_2O \cdot 1.7SiO_2$, and (at higher temperatures) $Na_2O \cdot 2SiO_2$, which have relatively weakly polymerized skeletons, formation of alkali in the solution leads to transfer also of SiO_2 from the protective surface layer in a molecularly dispersed form, and what may be regarded as dissolution of the glass occurs.

Change in temperature has a considerable influence on this secondary process: dissolution of silicic acid from the surface. Fig. 6 shows the variation with composition and temperature of the proportion *a* of silicic acid passing into solution when vitreous sodium silicates are treated with water for one hour. As will be seen from Figures 4 and 6, as the temperature rises the amounts of the components passing into solution increase considerably, and at the same time the boundary of the region of soluble silicates moves in the direction of higher silica content in the original glass.

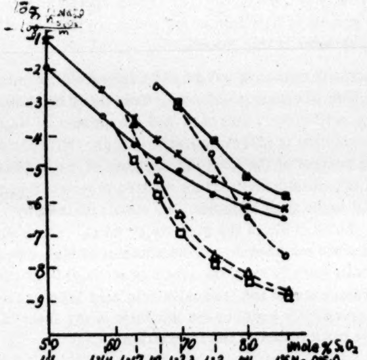

Fig. 4. Effect of composition on the amounts of the components going into solution when water acts on vitreous sodium silicates: —●— $\log n_{Na_2O}$, 40°, 1 hour; —x— $\log n_{Na_2O}$, 40°, 6 hours; —■— $\log n_{Na_2O}$, 100°, 1 hour; —□— $\log \frac{n_{SiO_2}}{m}$, 40°, 1 hour; —Δ— $\log \frac{n_{SiO_2}}{m}$, 40°, 6 hours; —o— $\log \frac{n_{SiO_2}}{m}$ 100°, 1 hour.

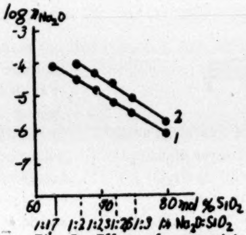

Fig. 5. Effect of composition on the amount of Na_2O going into solution when 0.1 N hydrochloric acid acts on sodium silicates: 1 - 1 hour; 2 - 6 hours.

The effect of hydrogen ion concentration on the transfer (resulting from the exchange) of sodium ions from the glass will be seen from a comparison of our results on leaching with water and with acid solutions. In the latter case a considerably greater amount of Na_2O passes into solution from the surface of the silicates investigated, and this is to be related to the marked rise in hydrogen ion

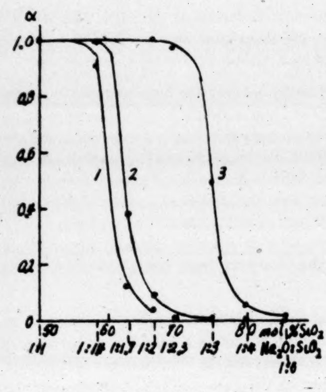

Fig. 6. Effect of composition and temperature on the proportion a of silicic acid going into solution in one hour when water acts on vitreous sodium silicates: 1) 25°; 2) 40°; 3) 100°.

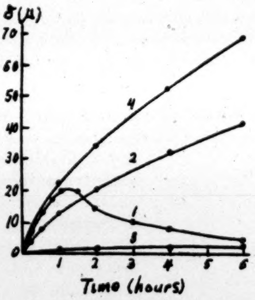

Fig. 7. Effect of the duration of treatment at 40° on the thickness of the residual layer of silicic acid on certain sodium silicates: 1) $Na_2O \cdot 1.7 SiO_2$ in water; 2) $Na_2O \cdot 2SiO_2$ in water; 3) $Na_2O \cdot 4SiO_2$ in water; 4) $Na_2O \cdot 2SiO_2$ in 0.1 N HCl.

concentration on passing from water to the acid solutions. Change in the concentration of the attacking acid in the range 0.01 N to 1N does not correspond to such a marked change in hydrogen ion concentration, and for this reason no significant difference in the leaching of the silicate $Na_2O \cdot 2.6 SiO_2$, treated with these acids is to be observed. As indicated above, the action of the acid solutions on the silicates under investigation is accompanied by leaching. The alkali that passes into solution has little effect on the hydrogen ion concentration, because of the large excess of acid used. Solutions in which the hydrogen ion concentration is high encourage the polymerization of silicic acid and have a feeble effect on the protective surface layer; in the case of the acid treatments, therefore, no silicic acid is to be detected in the solution, even for silicates having particularly high silica contents.

The residual silicic acid layer on the surface of sodium silicates changes in thickness with time in an extremely varied manner, depending on the initial composition and on the nature of the attacking reagent. This is illustrated by the curves in Fig. 7, which are calculated from the results given in Tables 4 and 5 from the formula given above.

In the case of $Na_2O \cdot 1.7 SiO_2$, the thickness of the residual layer increases rapidly at first, but later begins to diminish as a result of dissolution of silicic acid. In this case, therefore, the silicic acid film is unstable and is unable to protect the silicate from the action of the solution. This curve clearly shows also that the primary process is the passage of Na_2O into solution (more exactly: exchange of sodium ions of the glass for hydrogen ions of the solution). The dissolution of the residual film of silicic acid is mainly determined, however, by the alkalinity of the solution, and it lags appreciably in time behind the process of film formation, which is evidence of the secondary character of this process.

In experiments with sodium disilicate at 40°, continuous increase in film thickness is observed. Even this film, however, is evidently insufficiently compact, and the amount of Na_2O passing into solution is still comparatively high. With increase in the silica content of the glass the thickness of the residual silicic acid film diminishes, and its relative growth during the course of the experiment becomes less, as will be seen by considering the example of the glass $Na_2O \cdot 4SiO_2$. Since the action of aqueous solutions on sodium silicates of high silica content consists essentially in the leaching of Na_2O from the surface, the thickness of the residual silicic acid layer is in these cases practically equal to the thickness of the layer of glass that has participated in the interaction.

The residual silica layer on sodium silicate surfaces is thicker in the case of acid attack than in the case of attack by water. The protective action of this layer, however, depends not only on its thickness, but also on its structure, which is probably determined by the state of the silica in the original silicate. Increase in the silica content of sodium silicates evidently results in the strengthening of the sodium—oxygen linkages, i.e. in a reduction of the activity of the sodium ions in the glass, which reduces their tendency to pass from the glass to the solution.

SUMMARY

1. A study has been made of the action of water and hydrochloric acid solutions on vitreous sodium silicates having compositions corresponding to the invariant points on the phase diagram of the system Na_2O-SiO_2, to intermediate points, and also to points representing high silica contents.

2. The process of interaction of sodium silicates with water can be broken down into two stages: exchange of sodium ions of the glass for hydrogen ions of the solution, resulting in the formation of a residual layer of silicic acid, which together with the silica of the original glass comprises a protective film on the surface; and reaction of the protective layer with the alkaline solution that has been formed, resulting in removal of silicic acid from the surface by dissolution.

3. In the case of sodium silicates having a low silica content, a kinetic equilibrium is established between the primary and secondary reactions, so that dissolution of the glass appears to take place. In the case of sodium silicates of high silica content, the main process is the leaching of Na_2O from the glass.

4. When sodium silicates are treated with hydrochloric acid solutions, transfer to the solution of SiO_2 lags behind that of Na_2O to a greater extent than in the case of water treatments. In the case of glasses having a silica content greater than that of disilicate, no SiO_2 could be detected in the solution.

5. The relation between the logarithms of the amounts of components passing into solution and the molecular percentage of silica in the glass is represented over the range of compositions examined by smooth curves or (in the case of acid treatment) by straight lines, without appreciable deviations at compositions corresponding to invariant points on the phase diagram of Na_2O-SiO_2.

6. With rise in temperature the amounts of the components passing into solution increase considerably, and at the same time the boundary of the region of soluble silicates moves in the direction of glasses of higher original silica content.

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* See Consultants Bureau English translation, page 545.

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STATE OF SILICIC ACID IN SOLUTION, AND METHODS FOR ITS COLORIMETRIC DETERMINATION

M. M. Piryutko and Yu. A. Shmidt

The colorimetric determination of silicon based on the formation of a yellow silicomolybdate complex $H_8[Si(Mo_2O_7)_6]$ has recently come into wide use [1, 2]. Nevertheless, in spite of the large number of investigations devoted to the method of determining silicic acid, the question of the effect of the form in which the silicic acid is present in the solution on the results of the colorimetric determination has as yet received inadequate study.

Silicic acid may exist in solution both as comparatively simple ions or molecules and as more complex polymeric particles that are colloidally dispersed. According to the conditions, the equilibrium between these forms may be displaced in one or the other direction. There are indications in the literature that the colorimetric determination of silicic acid with ammonium molybdate is possible only in the first case: colloidal silicic acid cannot be completely determined by the use of the usual procedure. Although this circumstance may be highly significant in the colorimetric determination of silicic acid, it is not always taken into account.

The present work was undertaken in conjunction with other investigations that are proceeding at the Institute, which demand a method for the determination of small amounts of silicic acid in solutions of various composition and varying degrees of acidity. In order to solve this problem, we considered that it was necessary to study the conditions under which silicic acid passes into the "colorimetrically undeterminable" form and to verify the methods described in the literature for determining the total amount of silicic acid present in the solution, irrespective of its condition.

EXPERIMENTAL

For the determination of the silicic acid content of a solution we employed the following procedure. A definite volume of the solution to be tested was introduced into a 25 ml measuring flask and acidified with the amount of 2 N hydrochloric acid required to give a final concentration of about 0.1 N; 5% ammonium molybdate solution (1 ml) was added, the solution was made up to volume, and, after twenty minutes was examined colorimetrically on an FEK-M photoelectric colorimeter. The method gives results accurate within ± 2%.

Experiments designed to elucidate the effect of the degree of polymerization of the silicic acid on the results of the colorimetric determination were carried out as follows. Definite volumes of a standard sodium silicate solution prepared by dissolving the soda melt of a weighed amount of silica in water were acidified with definite amounts of hydrochloric acid. In this way, solutions having definite contents of silicic and hydrochloric acids were obtained. We expressed the concentration of silicic acid in terms of SiO_2 (g/ml), and it varied from 10^{-4} to 10^{-2} g/ml SiO_2. The concentration of hydrochloric acid varied over the range 0.1 N to 5 N. The solutions were kept in paraffined flasks, and samples were taken at definite intervals and were diluted to give solutions of concentration suitable for colorimetric examination.

Experiment showed that for SiO_2 concentrations of 10^{-4} g/ml and less, no conversion of silicic acid into the "colorimetrically undeterminable" form took place, irrespective of the acidity of the solution; i.e. no polymerization of the silicic acid occurred. At higher silicic acid concentrations, the amount actually found in the solution was usually less than the true amount. In the case of solutions containing $3\text{-}5 \cdot 10^{-4}$ g/ml SiO_2 and having a low hydrochloric acid concentration (0.1-0.2 N), there was a gradual diminution in the amount of silicic acid found in the solution by the colorimetric method. When the hydrochloric acid concentration was raised to 0.5 N and greater, the rate of conversion of silicic acid into the colorimetrically undeterminable form increased: there was a considerable fall in the amounts of silicic acid found during the first few days, and then these amounts remained practically constant for each value of the acidity (Fig. 1).

Experiments with concentrations of 10^{-3} - 10^{-2} g/ml SiO_2 showed that increase in silicic acid concentration led to an increased rate of conversion into the colorimetrically undeterminable form; this conversion occurs even at low acidity. In Fig. 2, curves are given that are characteristic of this range of silicic acid concentrations.

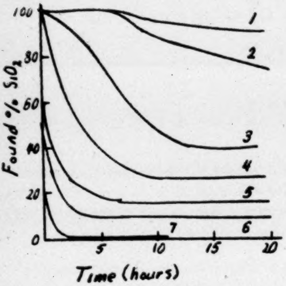

Fig. 1. Amount of silicic acid found colorimetrically in acid solutions expressed as a percentage of the true concentration ($5 \cdot 10^{-4}$ g/ml SiO$_2$). Concentration of hydrochloric acid: 1) 0.1 N; 2) 0.2 N; 3) 0.5 N; 4) 1 N; 5) 2 N; 6) 3 N; 7) 5 N.

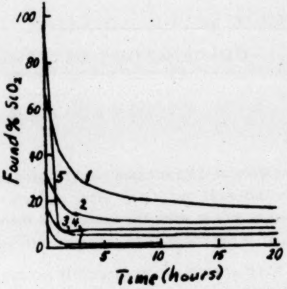

Fig. 2. Amount of silicic acid found colorimetrically in acid solutions expressed as a percentage of the true concentration ($2 \cdot 10^{-3}$ g/ml SiO$_2$). Concentration of hydrochloric acid: 1) 0.1 N; 2) 0.5 N; 3) 2 N; 4) 5 N; 5) neutral solution.

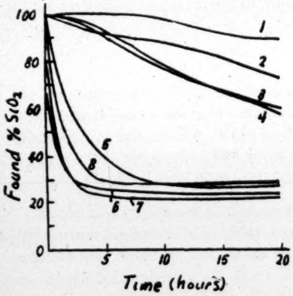

Fig. 3. Effect of salts on the amount of silicic acid found by colorimetric determination in acid solutions (true concentration, $5 \cdot 10^{-4}$ g/ml SiO$_2$): 1) 0.1 N HCl; 2) 0.1 N HCl + $3.8 \cdot 10^{-2}$ g/ml AlCl$_3$; 3) 0.1 N HCl + $4 \cdot 10^{-2}$ g/ml CaCl$_2$; 4) 0.1 N HCl + $4 \cdot 10^{-2}$ g/ml NaCl; 5) 1 N HCl; 6) 1 N HCl + + $3.8 \cdot 10^{-2}$ g/ml AlCl$_3$; 7) 1 NHCl + $4 \cdot 10^{-2}$ g/ml CaCl$_2$; 8) 1 N HCl + + $4 \cdot 10^{-2}$ g/ml NaCl.

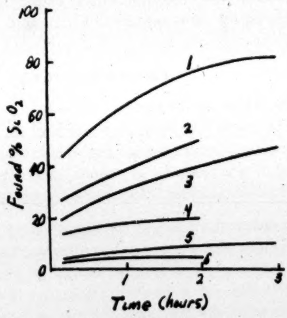

Fig. 4. Increase in intensity of color with time after addition of reagents (true concentration, $2 \cdot 10^{-3}$ g/ml SiO$_2$): 1) 0.1 N HCl after one day; 2) 0.1 N HCl after four days; 3) 0.5 N HCl after one day; 4) 0.5 N HCl after four days; 5) 3 N HCl after one day; 6) 3 N HCl after four days.

Experiments with a solution adjusted as closely as possible to give a neutral reaction showed that this behaved quite differently from the other solutions: already after one day, flocs appeared in the solution. Colorimetric analysis was able to account for only 7% of the original amount of silicic acid.

In order to investigate the effect of the chlorides of sodium, calcium, and aluminum on the rate of conversion of silicic acid into the colorimetrically undeterminable form, four series of solutions were prepared. In all these solutions the silicic acid concentration was $5 \cdot 10^{-4}$ g/ml; acidities of 0.1 N, 0.5 N, and 1 N were employed. Also, solutions of the second series contained $4 \cdot 10^{-2}$ g/ml of NaCl, those of the third series contained $4 \cdot 10^{-2}$ g/ml CaCl$_2$, and those of the fourth series $3.8 \cdot 10^{-2}$ g/ml AlCl$_3$.

The results of these experiments, which are shown in Fig. 3, indicate that in solutions of low acidity the presence of salts leads to an increase in the rate at which silicic acid is converted into the colorimetrically undeterminable form and to an increase in the proportion of silicic acid that is to be found in this form. At higher acidities (up to 1 N), the effect of salts is confined to a certain acceleration of the polymerization process; they are practically without effect on the equilibrium state.

We see, therefore, that for each value of the acidity an equilibrium is set up after a certain time between the colorimetrically determinable and undeterminable forms of silicic acid, and this then continues practically unchanged.

The concentration of determinable silicic acid at equilibrium depends, as will be seen from the results given in Table 1, on the acidity of the solution, and does not depend on the initial concentration of silicic acid.

When silicic acid solutions that have not been aged in acid solution are examined colorimetrically, the coloration attains a maximum intensity in 15-20 minutes after addition of the reagents and then remains constant for a definite period of time. We have found, however, that in the determination of silicic acid in aged acid solutions the colorations resulting from the addition of reagents increases constantly in intensity.

In order to investigate this phenomenon, special experiments were carried out, and the results of these are given in Fig. 4. As the solutions aged, the rise in the intensity of color became less marked. Increase in the acidity of the solution also caused a decrease in the rate at which the intensity of color increased. Reduction of the initial silicic acid concentration had a similar effect.

TABLE 1

Equilibrium Concentrations of Colorimetrically Determinable Silicic Acid in Acid Solutions

Conc. of SiO_2 (g/ml)	$3 \cdot 10^{-4}$		$5 \cdot 10^{-4}$		$1 \cdot 10^{-3}$		$2 \cdot 10^{-3}$	
Acidity of solution (normality)	Found SiO_2							
	%	$g/ml \cdot 10^{-4}$	%	$g/ml \cdot 10^{-4}$	%	$g/ml \cdot 10^{-4}$	%	$g/ml \cdot 10^{-4}$
0.1	–	–	87	4.4*	–	–	16	3.2
0.2	–	–	74	3.7*	–	–	14	2.8
0.5	–	–	39	1.95	20	2.03	10	2.00
1.0	~ 50	~ 1.5	27	1.35	14	1.38	7	1.40
2.0	28	0.83	17	0.85	8	0.77	4	0.80
3.0	–	–	9	0.45	–	–	2	0.40

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* Equilibrium was not attained.

If the solution is diluted and then kept for several hours before adding the reagents, the intensity of the coloration is somewhat greater than that in solutions to which the reagents are added immediately after the dilution. With increase in acidity or time of aging, this increased-intensity effect becomes appreciably less marked. Since the intensity of color obtained in the colorimetric test on aged acid solutions increases continuously with time, the comparisons between the experiments were always made on the basis of results obtained twenty minutes after the addition of the reagents.

The results of these experiments show that silicic acid undergoes polymerization in acid solution, i.e. it is transformed from the molecularly dispersed to the colloidally dispersed form (which explains the reductions in the amounts of silicic acid found in solution by the colorimetric method). The equilibrium between the molecularly dispersed and the colorimetrically undeterminable colloidally dispersed forms of silicic acid is not stationary, but moves toward a limit determined mainly by the acidity of the medium.. Introduction into the solution of ammonium molybdate leads to the binding of the molecularly dispersed silicic acid in the silicomolybdate complex, and, as a result, the equilibrium may be displaced by the conversion of part of the colloidal silicic acid into the colorimetrically determinable form. Since the amount of silicic acid present in the colloidal form is comparatively great, the conversion of a small part of it into the colorimetrically determinable form will cause an appreciable increase in the intensity of color, although the amount now found will nevertheless remain appreciably less than the true silicic acid content.

As the concentration of silicic acid is increased, the amount present in the colloidal form increases, and this circumstance favors a rise in the intensity of color during the course of the determination. On the other hand, increase in acidity and aging of the solution probably lead to the formation of larger complexes that are more difficult to break down, and, as a result, the rate of increase of color intensity diminishes with time. The colorimetric determination does not, of course, permit a strictly quantitative characterization of the ratio of the amounts of molecularly dispersed and colloidally dispersed forms of silicic acid, for the determination itself leads to a certain displacement of the equilibrium between them. It must be remembered also that a continuous series of intermediate states exists in the solution between these extreme states. It is also impossible , therefore, to draw any quantitative conclusions concerning the degree of polymerization of the silicic acid present in the colloidally dispersed condition on the basis of the colorimetric determination.

TABLE 2

Determination of the True Silicic Acid Content of an Aged Acid Solution by Adding Sodium Carbonate and Heating (SiO_2 concentration, $1 \cdot 10^{-3}$ g/ml; acidity as 1 N HCl)

Time (days)	SiO_2 found g/ml·10^{-3}	
	Direct determination	After addition of soda
1	0.240	1.03
		0.97
2	0.190	1.00
		1.01
5	0.185	1.02
		0.98
10	0.158	1.01
		1.03
15	0.142	0.99
		0.99
24	0.138	1.00
		1.03
30	0.138	1.01
		0.99

TABLE 3

Determination by Adding Caustic Soda and Heating, of the True Silicic Acid Content of an Acid Solution Aged in the Presence of Aluminum. (SiO_2 concentration, $1 \cdot 10^{-3}$ g/ml; Al_2O_3 concentration, $5 \cdot 10^{-3}$ g/ml; acidity as 1 N HCl.

Time (days)	SiO_2 found g/ml·10^{-3}	
	Direct determination	After addition of caustic soda
1	0.26	1.05
		1.05
3	0.20	1.02
		0.98
7	0.18	1.00
		1.00
10	0.16	1.01
		0.99
15	0.16	1.00
		1.00

Nevertheless, comparisons based on the results of colorimetric determinations permit us to draw a number of conclusions concerning the aging of acid solutions of silicic acid and the effect of a number of factors on this aging process. It should be noted also that our conclusions agree well with the electron-microscope investigations of SiO_2 sols carried out by Berestneva and Kargin [4].

It follows, therefore, that the colorimetric determination of silicic acid does not always reveal its true concentration. In order to determine the whole of the silicic acid in solution, irrespective of the form in which it is present, it is necessary to give the solution an additional treatment. Methods are described in the literature based on heating the solution with an addition of $NaHCO_3$ [1] or sodium fluoride [5]. In our work we heated the solutions after the addition of sodium carbonate or caustic alkali. The first method has the advantage that it is easier to obtain sodium carbonate of sufficiently low silicic acid content. On the other hand, the evolution of CO_2 when the solution is made alkaline with sodium carbonate (and all the more with $NaHCO_3$) and when it is reacidified before the determination makes some of the operations difficult, and treatment of the solution with caustic alkali is free from this defect.

TABLE 4

Determination, by Adding Sodium Fluoride, of the True Silicic Acid Content of Acid Solutions Aged in the Presence of Calcium, Aluminum, or Iron Compounds (SiO_2 concentration, $5 \cdot 10^{-4}$ g/ml; acidity as 1 N HCl)

Conc. of interfering substances	Time (days)	SiO_2 found (g/ml·10^{-4})	
		before treatment with NaF	after addition of NaF
0	4	2.50	5.05
	7	1.75	4.95
	9	1.60	5.00
$1 \cdot 10^{-2}$ g/ml $CaCl_2$	4	2.20	4.90
	7	1.70	4.90
	9	1.50	4.95
$2 \cdot 10^{-3}$ g/ml Al_2O_3	4	2.20	5.00
	7	1.65	4.90
	9	1.40	4.85
$2 \cdot 10^{-3}$ g/ml Fe_2O_3	4	2.40	5.00
	7	1.75	5.10
	9	1.75	4.90

The following is our procedure for the determination of silicic acid when it is partly present in the colorimetrically undeterminable form: the solution under investigation is neutralized in a platinum crucible with a solution of sodium carbonate or caustic alkali, and a further, excess amount is added, sufficient to bring the concentration to 0.1–0.2 N. If the solution contains a large amount of sodium chloride (up to 8%), the amount of alkali added must be increased to give a concentration of 0.5–0.8 N. The pipet used for the alkali must be carefully washed immediately with distilled water, as otherwise high results will be obtained in subsequent determinations. The solution is heated for 8–10 minutes on a water bath, and, after being cooled, it is acidified in the crucible so that the final acidity is about decinormal; it is then transferred to a measuring flask, where, after addition of reagent, it is made up to volume. In the simultaneous blank test, heating is not necessary; the necessary amount of acid is introduced into a measuring flask, the same amount of alkali is added as for the solution under investigation, and then ammonium molybdate is added. The solutions of sodium carbonate or caustic alkali must be tested for their silicic acid contents and must be kept in paraffined flasks. Silver crucibles may be used instead of platinum, but they must be boiled out with water before a determination to remove traces of silver oxide formed on the surface.

The method was checked on pure silicic acid solutions, and it was found that silicic acid could be quite satisfactorily determined, irrespective of the form in which it was present. In the case of a solution of $1 \cdot 10^{-2}$ g/ml SiO_2 in 1 N HCl, we found that even when the solution, as a result of aging, acquired a strong opalescence, colorimetric determination after treatment with sodium carbonate gave correct results. As an example we will give the determination of silicic acid during the course of the aging of one of the solutions (Table 2). The agreement of the results obtained with the initial concentration is satisfactory, although direct determination gave very low values.

We obtained similar results also for all the other concentrations of silicic and hydrochloric acids. The method was found to be accurate within approximately ±3%.

The question becomes a much more complicated one when, in addition to silicic acid, compounds of other elements are present in the solution. The method of converting silicic acid into a colorimetrically determinable form must then be selected taking into consideration the behavior of the individual elements during the treatment given to the solution. For example, correct results are not obtained when the solution contains aluminum and is treated with sodium carbonate, because the aluminum hydroxide that is then precipitated prevents complete conversion of the silicic acid into the colorimetrically determinable form (part of it being carried down with the precipitate). However, addition of caustic alkali in amount sufficient for the complete dissolution of the aluminum hydroxide makes it possible to obtain quite satisfactory results. Some of the results obtained in this case are given in Table 3.

Treatment of the solution with caustic alkali does not always give satisfactory results: it is not applicable when the solution contains ions that are precipitated by caustic alkali (iron, titanium, manganese, etc.). We therefore, carried out experiments on the conversion of silicic acid into the colorimetrically determinable form with the aid of sodium fluoride, which reacts with polymerized SiO_2 molecules in an acid medium forming fluosilicic acid, which is able to react with ammonium molybdate. The excess of fluoride ions, which interfere in the determination of silicic acid, must be fixed by addition of boric acid or aluminum ions.

The experiments were carried out as follows: the solution containing silicic acid in the colorimetrically undeterminable form (about 12 ml) was placed in a small paraffined beaker, and 2 N HCl (1.2 ml) and a 2.5% solution of sodium fluoride (1.5 ml) were added. After ten minutes, a solution (2.5 ml) containing $3 \cdot 10^{-3}$ g/ml $AlCl_3$ (to bind the excess of fluorine ions) and 5 % ammonium molybdate (2 ml) were added; the solution was transferred to a 25 ml measuring flask, made up to volume, and examined colorimetrically. Our method differs from that described in the literature [5] in that all operations are carried out at room temperature. The results given in Table 4 show that this procedure enables silicic acid to be determined in acid solutions in presence of calcium, aluminum, and iron salts.

SUMMARY

1. In acid solutions, polymerization of silicic acid occurs, and this results in a reduction in the amount that can be found by colorimetric analysis. An equilibrium between molecularly dispersed and colorimetrically undeterminable forms of silicic acid is established in accordance with the acidity of the medium. The presence in the solution of sodium, calcium, or aluminum chloride increases the rate at which equilibrium is established, but is practically without effect on its position.

2. In the colorimetric analysis of solutions containing silicic acid partly in the undeterminable form, a continuous increase with time in the intensity of color is to be observed. This is to be explained by the partial displacement of the equilibrium in the direction of the molecularly dispersed form brought about by the addition of ammonium molybdate.

3. In order to determine silicic acid in those cases when it is present in solution in the polymeric form, it is necessary first to convert it into the molecularly dispersed form. In order to achieve this we have heated the solutions with sodium carbonate or with caustic alkali, and we have also made use of addition of sodium fluoride at room temperature All three methods gave quite satisfactory results. The choice of one or another of these methods depends on the nature of the other substances present in solution.

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LIMITING CURRENTS ASSOCIATED WITH THE CATALYTIC DISCHARGE OF HYDROGEN IONS IN PRESENCE OF AMINES

COMMUNICATION 1. THEORY OF LIMITING CATALYTIC CURRENTS ASSOCIATED WITH THE DISCHARGE OF HYDROGEN IONS

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The term "catalytic evolution of hydrogen" is to be understood as the discharge of hydrogen ions at an electrode at potentials that are less negative than those usually required at the given electrode and at the given pH. The catalytic current results from the lowering of the overvoltage in presence of certain substances, i.e. catalysts.

A large number of investigations has been devoted to the experimental study of catalytic hydrogen waves at the dropping mercury electrode. Kolthoff and Lingane in their monograph [1] have made a review of work published up to 1940 on the catalytic action of a number of alkaloids and of substances containing a thiol group. A considerable number of alkaloids has been investigated polarographically by Kirkpatrick [2], and the catalytic evolution of hydrogen in presence of nicotinamide and other pyridine derivatives has been studied in detail by Knobloch [3], who found that the variation of the height of the catalytic wave with catalyst concentration follows an equation that is analogous to Langmuir's adsorption isotherm. He suggested that the catalytic current is proportional to the amount of catalyst adsorbed on the electrode. Experiment shows that when the concentration of catalyst in the solution reaches a certain value the height of the catalytic wave attains a maximum value and remains constant when the concentration is increased further. Knobloch attributes this effect to the complete saturation of the surface of the dropping electrode with catalyst molecules. It is not clear, however, why differing numbers of catalyst molecules are required for the filling of one and the same surface at various concentrations of the proton donor. Knobloch did not explain also the departure that he had observed of the theoretically calculated current from that found experimentally for low concentrations of catalyst.

The Soviet worker Stromberg [4] was the first to make use of the concept of kinetic and adsorption restrictions on the limiting current in order to describe the catalytic waves of hydrogen. His theory explains the behavior of the catalytic system: substance having a thiol group — metal ions — complex-former. Stromberg, however, gave no quantitative experimental confirmation of this theory.

A large amount of factual material has been collected on the catalytic evolution of hydrogen, but investigations of the catalytic current have been carried out over an insufficiently wide range of proton-donor and catalyst concentrations. This has made it impossible to develop a theory that would explain all the phenomena to be observed in the catalytic discharge of hydrogen ions.

We have investigated the relations between the limiting catalytic current and donor and catalyst concentrations over wide ranges of values, and, on the basis of the results, we have made an attempt to give a quantitative interpretation of the regularities observed. In these considerations we have taken the kinetics into account of those processes [5] which, in our opinion, take place at the surface of the dropping mercury electrode.

In the present paper we give the theory of limiting catalytic currents. The experimental results will be given in a later communication.

Derivation of Equations for Limiting Catalytic Currents

The catalytic current usually has a greater value than that to be expected for a simple process of catalyst molecule discharge, limited by diffusion. Every catalyst molecule, therefore, must deal with several proton-donor ions.

The mechanism of the catalytic discharge of hydrogen ions at the dropping mercury electrode may be represented as follows. The catalyst, which exists in two forms in equilibrium — Brønsted's acid and basic forms, BH^+ and B — has the role of proton carrier:

$$B + DH^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} BH^+ + D. \qquad (I)$$

The acid form of the catalyst BH^+ accepts electrons from the cathode and is converted into a discharged complex consisting of the basic form carrying a hydrogen atom (BH):

$$BH^+ + e^- \longrightarrow BH. \qquad (II)$$

There follows a process that results in the formation of a hydrogen molecule and regeneration of the catalyst in the basic form:

$$2BH \xrightarrow{k_3} 2B + H_2. \qquad (III)$$

If there are proton-donor ions DH^+ at the electrode surface, they will react with the basic form of the catalyst according to Equation I in an effort to re-establish the equilibrium concentration of the acid form, which is quickly discharged at the electrode; the whole cycle is then repeated. The values of the constant for the equilibrium between the acid and basic forms and the constant k_1 for the rate of formation of the acid form depend on the nature of the catalyst and of the proton donor. The constant k_3 depends only on nature of the catalyst. It will be obvious that the catalytic effect can occur only when the acid form of the catalyst is discharged at a lower negative potential than the proton donor.

The rates of the changes in concentration of the individual forms of the catalyst at the surface of the dropping electrode are described by the following equations:

$$\frac{d[B]_s}{dt} = \frac{\varkappa_B}{sF}\left([B]_0 - \frac{[B]_s}{a_B}\right) + k_3[BH]_s^2 - k_1[B]_s[DH^+]_s + k_2[BH^+]_s[D]_s. \qquad (1)$$

$$\frac{d[BH^+]_s}{dt} = \frac{\varkappa_{BH^+}}{sF}\left([BH^+]_0 - \frac{[BH^+]_s}{a_{BH^+}}\right) + k_1[B]_s[DH^+]_s - \frac{i}{sF} - k_2[BH^+]_s[D]_s, \qquad (2)$$

$$\frac{d[BH]_s}{dt} = \frac{i}{sF} - k_3[BH]_s^2 - \frac{\varkappa_{BH}}{sFa_{BH}}[BH]_s. \qquad (3)$$

In these equations $[Z]_0$ and $[Z]_s$ are the bulk and surface concentrations of the substances; $\varkappa_Z = 607\, D_Z^{1/2} m^{2/3} t^{1/6}$ is the constant of the Ilkovic equation; s is the mean surface of the dropping electrode; F is the faraday; a_Z is the constant for the equilibrium between the surface and bulk concentrations of the substance [6]:

$$a_Z = \frac{[Z]_s}{[Z]_0}, \qquad (4)$$

and i is the catalytic current.

An analogous equation can be written for the proton donor:

$$\frac{d[DH^+]_s}{dt} = \frac{\varkappa_{DH^+}}{sF}\left([DH^+]_0 - \frac{[DH^+]_s}{a^*_{DH^+}}\right) - k_1[B]_s[DH^+]_s + k_2[BH^+]_s[D]_s. \qquad (5)$$

In this equation $a^*_{DH^+}$ is not a constant, the point being that the concentration of proton donor is generally many times as great as the concentration of catalyst (often of quite a different order), and it frequently attains fairly high values (up to 0.1 M). In this case it is necessary to take into account the part of the surface occupied by the proton donor, and for the expression of its surface concentration the Langmuir equation must be used; thus:

$$a^* = \frac{a_{DH^+}}{1 + b[DH^+]_0}. \qquad (6)$$

At low values of $[DH^+]_0$ the value of $a^*_{DH^+}$ coincides with that of a_{DH^+}, which is a constant (Henry's constant).

When constant conditions are established at the surface of the drop, we have

$$\frac{d[Z]_s}{dt} = 0. \qquad (7)$$

For a limiting catalytic current there will be a further supplementary relationship: the concentration of the acid form at the electrode surface will fall to zero, which is described by the equation

$$[BH^+]_s = 0. \qquad (8)$$

Adding Equations 1, 2, and 3, while taking Equations 7 and 8 into account, we obtain

$$[B]_s = \frac{a_B}{\kappa_B}\left(\kappa_B[B]_0 + \kappa_{BH^+}[BH^+]_0\right) - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s. \tag{9}$$

For practical purposes we may consider [6] that

$$\kappa_B = \kappa_{BH^+}, \tag{10}$$

and we then have

$$[B]_s = a_B\left([B]_0 + [BH^+]_0\right) - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s = a_B\,[K]_0 - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s, \tag{11}$$

where $[K]_0$ is the general (analytical) concentration of catalyst in the solution.

For the surface concentration of proton donor we obtain from Equations 2 and 5:

$$[DH^+]_s = \frac{a^{\bullet}_{DH^+}}{\kappa_{DH^+}}\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0 - i\right). \tag{12}$$

Substituting the values for $[B]_s$ and $[DH^+]_s$ in Equation 2, and taking the conditions expressed in Equations 7 and 8 into account, we find that:

$$\frac{i}{sF} = \frac{\kappa_{BH^+}}{sF}[BH^+]_0 + \frac{k_1 a_B a^{\bullet}_{DH^+}}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0 - i\right), \tag{13}$$

whence

$$i = \frac{\kappa_{BH^+}[BH^+]_0 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0\right)\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)} \tag{14}$$

Taking into account the fact that the catalyst concentration is usually a hundred or a thousand times lower than the proton-donor concentration, i.e. that

$$[K]_0 \lll [DH^+]_0, \tag{15}$$

we may neglect the magnitude of the diffusion current for the acid form of the catalyst $\kappa_{BH^+}[BH^+]_0$ both in comparison with the magnitude of the diffusion current of the proton donor (the term $\kappa_{DH^+}[DH^+]_0$) and in comparison with the catalytic current, i.e. with the second term of the numerator of Equation 14. The expression for the magnitude of the limiting catalytic current will then take the form:

$$i = \frac{k_1 a_B a^{\bullet}_{DH^+}sF\,[DH^+]_0\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left([K]_0 \quad \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)} \tag{16}$$

A similar expression is obtained when, as is often the case, the catalytic wave precedes the wave for the reduction ("hydrogenation") of the catalyst itself.

Let B' and B'H$^+$ be the basic and acid forms of the unreduced catalyst. If we assume that the acid form, owing to the difference in charges, is more readily reduced, then at the electrode, the following processes precede the catalysis:

$$B' + DH^+ \xrightarrow{k_4} B'H^+ + D \tag{IV}$$

and

$$B'H^+ + (n-1)\,H^+ + ne^- \xrightarrow{i_{\text{hydr.}}} B. \tag{V}$$

In acid solution the catalyst is present mainly in the acid form, and for the diffusion wave associated with "hydrogenation" of the catalyst we may write

$$i_{\text{hydr.}} = n\kappa_B[K]_0. \tag{17}$$

The factor n is introduced because in Equations 1, 2, and 3 κ_B took only the rate at which the substance was presented into account and n was assumed to be unity.

Equations I, II, and III will be correct for the catalytic process. The rate of change in the concentrations of the individual substances at the cathode will be given by the equations:

$$\frac{d[B]_s}{dt} = \frac{i_{hydr.}}{nsF} + k_3[BH]_s^2 + k_2[BH^+]_s[D]_s - k_1[B]_s[DH^+]_s - \frac{\kappa_B}{sF}\frac{[B]_s}{a_B}, \tag{18}$$

$$\frac{d[BH^+]_s}{dt} = k_1[B]_s[DH^+]_s - \frac{i}{sF} - k_2[BH^+]_s[D]_s - \frac{\kappa_{BH^+}}{sF}\frac{[BH^+]_s}{a_{BH^+}}, \tag{19}$$

$$\frac{d[BH]_s}{dt} = \frac{i}{sF} - k_3[BH]_s^2 - \frac{\kappa_{BH}[BH]_s}{sFa_{BH}}, \tag{20}$$

$$\frac{d[DH^+]_s}{dt} = \frac{\kappa_{DH^+}}{sF}\left([DH^+]_0 - \frac{[DH^+]_s}{\dot{a}_{DH^+}}\right) - k_1[B]_s[DH^+]_s - \frac{i_{hydr.}}{sF} + k_2[BH^+]_s[D]_s. \tag{21}$$

By taking the conditions expressed in Equations 7 and 8 into account we obtain from Equation 19:

$$i = k_1 sF[B]_s[DH^+]_s. \tag{22}$$

It follows from Equations 18, 19, 21, and 22 that:

$$[B]_s = \frac{i_{hydr.}\cdot a_B}{n\cdot\kappa_B} - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}[BH]_s \tag{23}$$

and

$$[DH^+]_s = \dot{a}_{DH^+}[DH^+]_0 - \frac{\dot{a}_{DH^+}}{\kappa_{DH^+}}(i + i_{hydr.}). \tag{24}$$

Substituting Equations 23 and 24 in Equation 22, we find

$$\frac{i}{sF} = k_1 a_B \dot{a}_{DH^+}\left([DH^+]_0 - \frac{i + i_{hydr.}}{\kappa_{DH^+}}\right)\left(\frac{i_{hydr.}}{n\kappa_B} - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right) \tag{25}$$

and

$$i = \frac{k_1 a_B \dot{a}_{DH^+} sF\left([DH^+]_0 - \frac{n\kappa_B[K]_0}{\kappa_{DH^+}}\right)\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \frac{k_1 a_B \dot{a}_{DH^+} sF}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}. \tag{26}$$

If Equation 15 holds, then, neglecting $n\kappa_B[K]_0/\kappa_{DH^+}$ in comparison with $[DH^+]_0$, we obtain:

$$i = \frac{k_1 a_B \dot{a}_{DH^+} sF[DH^+]_0\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \frac{k_1 a_B \dot{a}_{DH^+} sF}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}. \tag{27}$$

It will be readily seen that Equation 27 is identical with Equation 16.

In Equations 16 and 27 the value of the concentration $[BH]_s$ remains undetermined. An expression for $[BH]_s$ can be readily found from Equation 3:

$$[BH]_s^2 + \frac{\kappa_{BH}[BH]_s}{k_3 a_{BH} sF} - \frac{i}{k_3 sF} = 0. \tag{28}$$

and therefore

$$[BH]_s = -\frac{\kappa_{BH}}{2k_3 a_{BH} sF} + \sqrt{\left(\frac{\kappa_{BH}}{2k_3 a_{BH} sF}\right)^2 + \frac{i}{k_3 sF}}. \tag{29}$$

Only the positive sign is to be taken before the root, since the value of $[BH]_s$ cannot be a negative one. Allotting symbols to the constants:

$$\frac{\kappa^2_{BH}}{2k_s sF a^2_{BH}\kappa_B} = r \text{ and } \frac{4k_s a^2_{BH} sF}{\kappa^2_{BH}} = p, \qquad (30), (31)$$

we find that the expression $[BH]_s$ takes the form:

$$[BH]_s = \frac{\kappa_B a_{BH}}{\kappa_{BH}} \cdot r\left(\sqrt{1+ip}-1\right) \qquad (32)$$

Substituting the expression for $[BH]_s$ from Equation 32 and that for $\overset{*}{a}_{DH^+}$ from Equation 6 into Equation 16, we obtain a general equation relating the value of the catalytic current to the concentrations of the components of the solution:

$$i = \frac{k_1 a_B a_{DH^+} sF \kappa_{DH^+} [DH^+]_0 \quad \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}}{\kappa_{DH^+}(1 + b\ [DH^+]_0) + k_1 a_B a_{DH^+} sF \left\{[K]_0 + r\left(\sqrt{1+ip}-1\right)\right\}}. \qquad (33)$$

It is necessary to remember that for very low values of the ratio $[DH^+]_0 / [K]_0$ (10-100 or less), when the condition in Equation 15 does not operate, it is no longer possible to neglect the diffusion current for the discharge of the basic form of the catalyst or its "hydrogenation" current. It is then necessary to employ not Equation 33, but Equations 14 or 26, substituting in these the values of $\overset{*}{a}_{DH^+}$ and $[BH]_s$ from Equations 6 and 32. A low value of $[DH^+]_0/[K]_0$ is met in polarographic practice when working with catalytic waves in solutions of high pH. In this case the proton donor (most frequently the acid salt of a polybasic acid, or an ammonia buffer, in which the donor is NH_4^+) is fairly inert, and the rate (k_1) of its reaction with the catalyst is not great. Hence, in order to obtain values of the catalytic current that are convenient for measurement it is necessary to increase the concentration of the catalyst considerably.

Case of High Proton-Donor Concentrations

As a subsequent communication will show, for sufficiently high values of the ratio $[DH^+]_0/[K]_0$, the catalytic current does not depend on the concentration of the donor in the solution. The surface concentration of the donor is so great in this case that it covers an appreciable proportion of the electrode surface, and, owing to the low concentration of catalyst, the removal of donor from the surface due to catalytic discharge is not considerable.

If the concentration of acid is very much greater than that of catalyst, then in the denominator of Equation 33 we may neglect the terms κ_{DH^+} and $k_1 a_B a_{DH^+} sF \left\{[K]_0 - r(\sqrt{1+ip} - 1)\right\}$ in comparison with $b \cdot \kappa_{DH^+} [DH^+]_0$. The expression for the catalytic current then takes the form:

$$i = \frac{k_1 a_B a_{DH^+} sF}{b} \quad \{[K]_0 - r(\sqrt{1+ip}-1)\} \qquad (34)$$

or

$$i = Q\left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\} \qquad (35)$$

in which

$$Q = k_1 a_B a_{DH^+} sF/b. \qquad (36)$$

If at low catalyst concentrations the acid concentration is not sufficiently high, so that we may neglect only the term $k_1 a_B a_{DH^+} sF \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}$ in the denominator of Equation 33, then this equation will take the form:

$$i = \frac{k_1 a_B a_{DH^+} sF\ [DH^+]_0}{1 + b[DH^+]_0} \quad \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}, \qquad (37)$$

or

$$i = Q' \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}, \qquad (38)$$

where

$$Q' = \frac{b[DH^+]_0}{1 + b[DH^+]_0} Q. \qquad (39)$$

Conditions corresponding to this case are found in experiments in 0.05 N HCl, the results of which are given in the subsequent communication.

As will be shown, the value of the constant p for quinine is of the order of 10^5 microamp^{-1}. The two terms of unity in Equation 38 may therefore be neglected in comparison with the magnitudes of ip and $\sqrt{ip}$, for at currents of not less than 1 microamp we have:

$$ip \gg 1 \quad \text{and} \quad \sqrt{ip} \gg 1 \tag{40}$$

so that

$$i = Q'([K]_0 - \sqrt{r^2 ip}) \tag{41}$$

The equation for the current derived from Equation 41 is

$$i = Q'[K]_0 + \frac{(Q')^2 r^2 p}{2} - \sqrt{\frac{(Q')^4 r^4 p^2}{4} + (Q')^3 r^2 p\, [K]_0}. \tag{42}$$

The derivative of the current with respect to the catalyst concentration has the form:

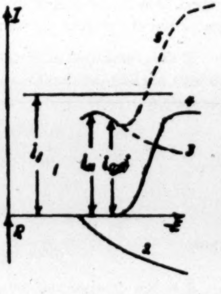
$$\frac{di}{d[K]_0} = Q' - \frac{(Q')^3 r^2 p}{\sqrt{(Q')^4 r^4 p^2 + 4(Q')^3 r^2 p\, [K]_0}} \tag{43}$$

and the slope of the curve i = f ($[K]_0$ therefore rises with increase in quinine concentration and tends toward the value Q'.

Form of the Catalytic Wave

A peculiar feature of catalytic waves is the presence on them of a convexity having a flat maximum followed by a concave depression. Catalytic waves do not change in character when surface-active substances are added to the solution. The nature of the maximum, therefore, is not associated with the movement of the mercury surface of the dropping electrode, but arises from the nature of the catalytic effect itself.

It should be noted that it has been assumed in this paper, as also in other papers cited [1,2,3], that the value of the limiting catalytic current corresponds to the height of the catalytic wave at its maximum. This assumption is a convenient one when catalytic waves are used for analytical purposes, but it is not theoretically justified. The catalytic wave can be represented as the sum of three curves (see Figure). Curve 1 is the "original" catalytic wave of the usual form. To this we must add algebraically Curve 2, which represents the dependence of $R = k_1 a_B a_{DH^+} sF$, on the potential (possible changes in the value of $\sqrt{r^2 p}$ with potential may be neglected, for rp is a constant, and the effect of the added constant $\sqrt{ri}$ is negligible). This relationship may be expressed in the form $R = Ae^{\beta(E_0 - E)}$, where E_0 is the potential at which R has its maximum value, and E is the cathode potential; A and β are constants. The superposition of Curves 1 and 2 determines the form of the catalytic wave, if the usual discharge of the proton donor does not follow immediately after the catalytic discharge. If immediately after the catalytic discharge there follows the usual discharge of the proton donor, which has not been discharged catalytically, then on the catalytic wave 3 there is superimposed the wave for the discharge of donor remaining on the electrode surface (Curve 4). A rise sets in on the catalytic curve (Curve 5), which goes over into the wave of the proton donor.



Scheme illustrating the form of the catalytic wave: 1) "original" catalytic wave; 2) curve of R against E; 3) catalytic wave without superposition of the discharge current of the donor; 4) wave for the discharge of the donor; 5) summation wave.

The value of the limiting catalytic current is a function of the potential, and its greatest value i_1 corresponds to maximum R. The current at the maximum of the observable wave, i_m, forms a certain proportion of i_1, and the ratio i_1/i_m depends on the relation between the concentrations of catalyst and donor. At high values of $[K]_0/[DH^+]_0$, as follows from Equation 46, change in R is practically without effect on the value of the limiting current, which is determined by supply of donor. The wave then does not have a maximum, and i_1/i_m has a minimum value. At low values of $[K]_0/[DH^+]_0$ the wave for the usual discharge of the donor begins at less negative potentials, the beginning of the rise fully compensates for the fall in the curve due to the fall in R, and the wave has the form of the usual S-shaped curve. The catalytic wave itself, however, which is obtained from the total wave by subtraction of the donor wave, shows its usual fall.

The author takes this opportunity of expressing his great indebtedness to M. B. Neiman for his constant interest in the work, and also to A. N. Frumkin for valuable suggestions.

SUMMARY

1. A kinetic interpretation has been given of the phenomena observed in the catalytic discharge of hydrogen ions.

2. Relationships have been derived between the value of the limiting catalytic current and the concentrations of the components of the solution.

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CONDITIONS FOR THE IGNITION OF GAS MIXTURES

COMMUNICATION 22. EFFECT OF ADDITIONS OF DIETHYL PEROXIDE AND ACETALDEHYDE ON THE KINETICS OF COOL-FLAME OXIDATION OF BUTANE

A. A. Dobrinskaya and M. B. Neiman

In a series of investigations, Neiman, Tutakin, Blat, and Gerber [1, 2] have studied the effect of the addition of diethyl peroxide on the period of induction of the butane cool flame. It was shown that the induction period for the butane cool flame depends on the amount x of added peroxide, the relationship being expressed by the following equation:

$$K_1\tau = a - \ln x. \quad (1)$$

Neiman and coworkers [3, 4] have shown that this equation is applicable to the oxidation of propane and of dimethyl ether. Similar results were obtained by Egerton and Harris [5] in an investigation of the effect of diethyl peroxide on the induction period for the propane cool flame.

In the present investigation we have set ourselves the task of studying in greater detail the effect of diethyl peroxide on the process of cool-flame oxidation of butane and also of the effect on this process of acetaldehyde, the kinetics of the formation of active products during the induction period being investigated in each case. Studies of the kinetics, in absence of additives, of the build-up of active intermediate products during the period of induction of the butane cool flame have also been made previously [6, 7].

EXPERIMENTAL

Experimental Procedure

a) Description of apparatus. Apart from some minor modifications, the procedure followed was the same as that described in detail in previous papers [6, 7]. The cool flame was obtained by admitting a mixture of butane and oxygen into a previously evacuated quartz vessel heated to a definite temperature; the formation of flame was observed visually. Induction periods were determined with the aid of a stop watch. Analytical tests on the gaseous reaction mixture were made as follows. At a definite time the gaseous mixture was allowed to pass from the reaction vessel to an intermediate flask, and was slowly pumped off through a U-tube cooled by liquid oxygen. The condensed reaction products were then warmed and blown out with a stream of hydrogen into a train of two absorption vessels. The solutions were then analyzed polarographically for their content of organic peroxides and aldehydes [8-13].

b) Preparation and purification of the starting materials. Butane was prepared by the hydrogenation of 2-butene; it was purified from unsaturated hydrocarbons and tested for organic peroxides and aldehydes in the manner described in the literature [5]. Diethyl peroxide was prepared from diethyl sulfate and 12% hydrogen peroxide [14]. Diethyl sulfate (105 parts) and hydrogen peroxide (125 parts) were carefully mixed together in a flask at 15°. A 5% solution of KOH (180 parts) was added dropwise to the mixture. Reaction proceeded under careful cooling for six hours, and the reaction products were then fractionated on an oil bath. The fraction boiling between 55° and 76° was collected and was washed with a 30% solution of NaOH and with water in order to remove alcohol and ether. The diethyl peroxide obtained was repeatedly distilled; the fraction boiling between 63.5° and 65° was used in the experiments. The refractive index (n_D^{20}) of diethyl peroxide was found to be 1.37014, a value in good agreement with that found by Neiman, Blat, and Gerber, namely n_D^{20} = 1.37009 [2].

Measurements were made also of the vapor pressure of diethyl peroxide at various temperatures. The latent heat of vaporization of diethyl peroxide calculated from these results was λ=7400 cal/mole, in good agreement with the value of λ=7300 cal/mole obtained by Blat [2]. Acetaldehyde CH_3CHO was prepared by the depolymerization of pure paraldehyde, and was carefully fractionated. The fraction boiling at 20° was used in the experiments. In order

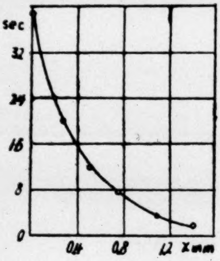

Fig. 1. Effect of addition of diethyl peroxide on the induction period for the butane cool flame.

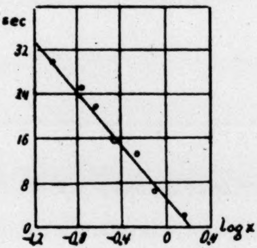

Fig. 2. Relation between the induction period for the butane cool flame and the concentration of diethyl peroxide.

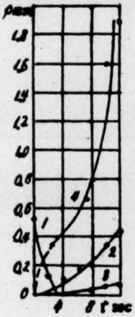

Fig. 4. Changes in the contents of diethyl peroxide (1), peroxides A and B (2 and 3), and aldehydes (4) during the induction period for the mixture $C_4H_{10} + O_2 + 0.5$ mm $(C_2H_5O)_2$ at 310° and 333 mm.

to avoid the formation of peroxides, the acetaldehyde was kept in sealed ampoules in absence of oxygen. Before an experiment, qualitative tests for peroxides were made, and the results were always negative. Oxygen and hydrogen were prepared by the electrolysis of a 15% solution of NaOH, and they were then purified as indicated in previous papers [6, 7].

EXPERIMENTAL RESULTS

1. Effect of Addition of Diethyl Peroxide on the Kinetics of Cool-Flame Oxidation of Butane

a) Shortening of the induction period due to addition of diethyl peroxide. We investigated the shortening of the induction period resulting from addition of diethyl peroxide at 310° and 333 mm. As will be seen from the curve (Fig. 1), as the addition of diethyl peroxide was increased, the period of induction was reduced in a regular manner.

In order to verify Equation 1, we plotted the experimental results with log x and τ as coordinates (Fig. 2), and, within the limits of experimental error, the experimental points fall on a straight line, as required by Equation 1. From the slope of this line we find $K = 0.009$.

b) Build-up of peroxides and aldehydes. We investigated the build-up of peroxides and aldehydes during the induction period, the reaction being carried out in presence of diethyl peroxide. In this series of experiments, carried out at 310° and 333 mm, an addition of 0.54 mm of diethyl peroxide was made to the butane-oxygen mixture. The amounts of peroxides and aldehydes were determined by a polarographic method, as described above. The results of our analyses are represented in Fig. 3.

It will be seen from Fig. 3 that the concentration of diethyl peroxide rapidly fell immediately after the admission of the mixture into the heated vessel. Simultaneously peroxides, which were reduced at -0.2 and -0.1V. (Curves 2 and 3) and aldehydes (Curve 4) began to accumulate in the mixture. The decomposition of diethyl peroxide resulted in the appearance of appreciable amounts of aldehydes, and many initiating centers were evidently formed. As as result, the oxidation reaction was accelerated.

2. Effect of Addition of Acetaldehyde on the Kinetics of Cool-Flame Oxidation of Butane

a) Shortening of the induction period due to addition of acetaldehyde. It has been shown by the work of Aivazov and Neiman [15] that addition of acetaldehyde leads to a shortening of the period of induction of the pentane cool flame. We have investigated the effect of addition of acetaldehyde on the period of induction of the cool flame of butane at 333 mm and 310°. As the addition of CH_3CHO was increased, the induction period for the cool flame was reduced in a regular manner (Fig. 4). Addition of CH_3CHO in amounts appreciably in excess of that which, according to our analyses, builds up by the end of the induction period, although shortening the induction period, did not eliminate it completely. Newitt and Thornes's hypothesis [16], according to which the cool flame arises as a result of the building up of a critical concentration of aldehydes, is therefore evidently incorrect.

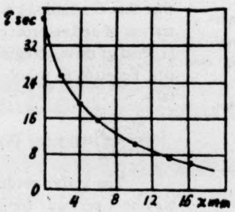

Fig. 4. Effect of addition of acetaldehyde on the kinetics of cool-flame oxidation of butane

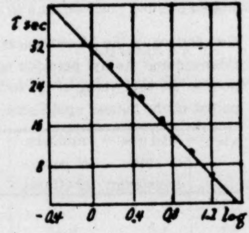

Fig. 5. Relation between the period of induction of the butane cool flame and the concentration of acetaldehyde

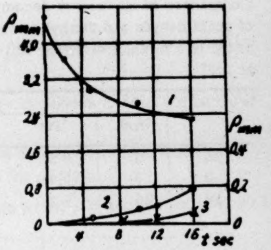

Fig. 6. Changes in the concentrations of aldehydes (1) and peroxides that are reduced at -0.25 and -0.6 v (2 and 3) during the induction period in the mixture C_4H_{10} (164 mm) + O_2 + $(C_2H_5O)_2$ (4.5 mm) at 310° and 333 mm.

The relation between the induction period and the amount of added aldehyde [Ald] closely accords with the equation

$$\log\ [\mathrm{Ald}] = b - 04343\ K_2\tau \qquad (2)$$

as will be seen from Fig. 5, in which the experimental results are plotted with log [Ald] and τ as coordinates The experimental points lie on a straight line, and it follows from the value of the slope of this line that b in Equation 2 has the value 0.1. The shortening of the induction period for the butane cool flame due to addition of acetaldehyde therefore follows the same law as that found for additions of diethyl peroxide.

The good quantitative agreement between the coefficients K_1 and K_2 of Equations 1 and 2 should be noted. The constants a and b in these equations differ in value.

b) Changes in the concentrations of peroxides and aldehydes We have carried out a series of experiments with the mixture $C_4H_{10}+O_2$ in presence of 4.5 mm of acetaldehyde In these experiments the pressure and temperature of the mixture were 333 mm and 320° respectively. The results of peroxide determinations for these conditions are given in Fig. 6. An examination of Fig. 6 will show that as the concentration of aldehyde in the mixture fell there was a simultaneous accumulation of peroxides, which were reduced at -0.25 and -0.6 V. The latter was formed to about double the extent of the former.

DISCUSSION OF RESULTS

We will examine the possible mechanism of cool-flame induction by additives. Our experiments give us reason to suppose that, when a certain amount of diethyl peroxide is added, the latter decomposes with formation of the peroxides A and B (which are reduced at -0.2 and -1.0 v).

We will suppose that the initial concentration of the peroxide formed is proportional to the rate of decomposition of diethyl peroxide, for which the constant is k_1; we may then write:

$$[\mathrm{Per}]_0 = k_1[\mathrm{Per}]_0' \qquad (3)$$

We shall make the same assumption in the case of the acetaldehyde addition. Let the constant for the decomposition of the aldehyde be k_2; the initial concentration of the peroxide will then be expressed in Equation 4:

$$[\mathrm{Per}]_0 = k_2[\mathrm{Ald}]_0 \qquad (4)$$

Blat, Gerber and Neiman [2] suppose that during the induction period there is a slow autocatalytic reaction, in the course of which active oxidation products are formed. The rate of formation of active products is expressed by the equation:

$$\frac{d[\mathrm{Prod}]}{dt} = K[\mathrm{Prod}] \qquad (5)$$

The cool flame arises when the concentration of active products attains a value termed by the authors "critical."

TABLE 1

Comparison of the rates of decomposition of acetaldehyde and diethyl peroxide added to a mixture of butane and oxygen at 310°

% decomp.	Time of decomp (sec)		$\frac{t_{Ald}}{t_{Per}}$
	t_{Ald}	t_{Per}	
25	3	0.2	15
33	6	0.4	15
50	20	1.2	16

TABLE 2

Comparison of the effectiveness of acetaldehyde and diethyl peroxide with respect to the shortening of the induction period of the butane cool flame

t(sec)	Addition of aldehyde(mm)	Addition of peroxide (mm)	$\frac{Ald}{Per}$
32	0.9	0.06	15
24	2.5	0.16	15
16	5.8	0.36	16
8	12.8	0.75	17
4	19.5	1.15	17

Let us suppose further that the initial concentration of active products is $[Prod]_0$; then, integrating Equation 5, we obtain:

$$\ln\frac{[Prod]_c}{[Prod]_0} = K\tau \qquad (6)$$

The active product may be a peroxide formed from the added diethyl peroxide.

Substituting the value of $[Per]_0$ from Equation 3 in Equation 6, we obtain:

$$\ln\frac{[Per]_c}{k_1[Per]'_0} = K\tau. \qquad (7)$$

In a similar way, substituting the value of $[Per]_0$ from Equation 4 in Equation 6, we obtain:

$$\ln\frac{[Per]_c}{k_2[Ald]'_0} = K\tau. \qquad (8)$$

From Equations 7 and 8 we shall determine the ratio of the peroxide and aldehyde concentrations that shorten the induction period to an equal extent.

If we treat the values of τ in Equations 7 and 8 as identical, we obtain by equating the left-hand side of these equations:

$$\ln\frac{[Per]_c}{k_1[Per]'_0} = \ln\frac{[Per]_c}{k_2[Ald]_0} \qquad (9)$$

It follows from this that there will be equal shortening of the period of cool-flame induction when the concentrations of the added aldehyde or peroxide are inversely proportional to their decomposition constants:

$$\frac{[Ald]_0}{[Per]_0} = \frac{k_1}{k_2} \qquad (10)$$

The ratios of the rate constants for the decompositions of acetaldehyde and diethyl peroxide may be determined from the ratio of the intervals of time during which these substances decompose to a definite extent.

$$\frac{k_1}{k_2} = \frac{t_2}{t_1} \qquad (11)$$

In Table 1, the intervals of time are given during which diethyl peroxide and acetaldehyde, admitted into a mixture of $C_4H_{10} + O_2$, decompose to the extent of 25%, 33%, and 50%. It can be seen from Table 1 that

$$\frac{t_{Ald}}{t_{Per}} = \frac{k_1}{k_2} \approx 15. \qquad (12)$$

This means that under the conditions of the experiments described the peroxide decomposes about fifteen times as rapidly as acetaldehyde

In Table 2, the amounts of aldehyde and peroxide are given which shorten the induction period for the cool flame to an equal extent.

The data on which Table 2 is based are taken from Figures 1 and 4.

As may be seen from Table 2:

$$\frac{[Ald]}{[Per]} \approx 16 \qquad (13)$$

The value of the ratio $\frac{[Ald]}{[Per]}$ calculated from our experiments coincides, within the limits of experimental error, with the ratio of their decomposition rates, as will be seen by comparing Equations 12 and 13.

The mechanism we have proposed for the shortening of the period of induction of the cool flame in presence of active additives is therefore able to give a satisfactory explanation of the observed facts.

SUMMARY

1. It has been shown that addition of diethyl peroxide to a butane-oxygen mixture reduces the period of induction of the cool flame.

2. When the additive is diethyl peroxide, organic peroxides and aldehydes are formed in the mixture during the induction period.

3. It has been shown that the addition of acetaldehyde shortens the period of induction of the butane cool flame. Organic peroxides, which are reduced at -0.25 and -0.6 V, are formed in the mixture.

4. Addition of an amount $\underline{x}$ of peroxide or aldehyde reduces the induction period τ in accordance with the law:

$$\log x = b - k\tau .$$

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NEW APPARATUS FOR MEASURING SORPTION

E. N. Nikitin

The high accuracy of sorption measurements, which has been attained largely as a result of the work of Academician M. M. Dubinin's school [1,2], permits satisfactory determinations to be made of the surface and porosity of gels and fine powders. Sorption measurements are carried out at the present time almost exclusively by a gravimetric or volumetric method in which a high vacuum is employed. Improvement in sorption apparatus has proceeded on the one hand in the direction of particularly sensitive balances, permitting the registering of changes in the weight of sorbent of less than 10^{-5} g; and on the other hand, the efforts of experimentalists have been directed toward the devising of apparatus for volumetric sorption measurements based on the measurement of pressure changes resulting from introduction of sorbent. The lower limit of applicability for the gravimetric method is determined by the sensitivity and capacity of the quartz spiral. The volumetric method has a wider range of applicability; it is most useful for the investigation of the surface area and porosity of sorbents of low activity.

Numerous designs for sorption apparatus have been published [3]. Below we give a description of yet another apparatus of simpler design, which, in our view, enables volumetric sorption measurements of increased accuracy to be made. Simplification of apparatus accompanied by increased accuracy should encourage the introduction of sorption technique into laboratory practice.

Volumetric Sorption Apparatus

The proposed apparatus combines in itself the elements of a McLeod gage, a U-type manometer, a gas buret, and a thermostated tube for sorbent (Fig. 1). Unlike existing apparatus [3], this device has no capillary communicating tubes: capillary tubes impede evacuation so much that it is probably rare for the adsorbent to be freed from sorbed impurities [4]. The principle on which the apparatus works is a generally accepted one and is based on the determination of the pressure change occurring in a space when a sorbent is introduced into it.

Mercury from the reservoir R can pass into the gage and compress gas in the left limb to a volume corresponding to a position in the capillary K. The mercury in the right limb will therefore stand at a higher level than in the left limb. The position of the mercury can be fixed with the aid of a stainless steel rod, the end of which is ground to act as a stopper. The volumes of the capillary and the left limb are determined by filling with mercury, so that the apparatus can serve as a McLeod gage.

In order that the apparatus may be used as a U-type manometer having a renewable vacuum, it is sufficient for the mercury to be raised about half-way in the two limbs. As the sorption measurements are carried out at a strictly constant volume, there is a sealed-in platinum contact at C. When the mercury comes in contact with the platinum, an electric circuit is closed and a small neon lamp flashes. The elevation of the mercury in the left limb is measured with the aid of a cathetometer fitted with a microscope and mechanical indicator I.

The whole space in the right limb above the fused-in contact is surrounded by a glass jacket A_1, through which water is circulated from an ultrathermostat. The volume of the space, V_1, is determined by filling with mercury, and this space may therefore act as a substitute for a gas buret. The tube containing adsorbent, V_2, may be connected to, or disconnected from the thermostated space V_1 by means of a tap. The volume of the tube V_2 is also determined by filling with mercury. While measurements are in progress, the tube V_2 is thermostated by surrounding it with the small glass jacket A_2; during evacuation the jacket A_2 is replaced by the tubular nichrome heater H.

In the upper part of the apparatus there is a three-way tap, which enables the apparatus to be connected either to the vacuum main or to a tube containing the liquid to be sorbed (e.g. methanol, ethanol, water, etc.). Glass inserts are placed in the nonthermostated tubing; these are intended to reduce the volume of nonthermostated space.

When graduating the apparatus it is convenient to determine the volumes in the left limb before the apparatus is attached to the evacuation system. The volumes V_1 and V_2 are determined by removing mercury with the aid of a Drechsel bottle attached to a water pump. This operation must be preceded by thorough evacuation of the whole apparatus followed by complete filling of the whole appratus with mercury (including the tube for the sorbent).

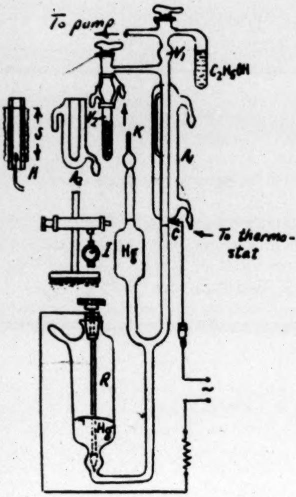

Fig. 1. Volumetric Sorption Apparatus.

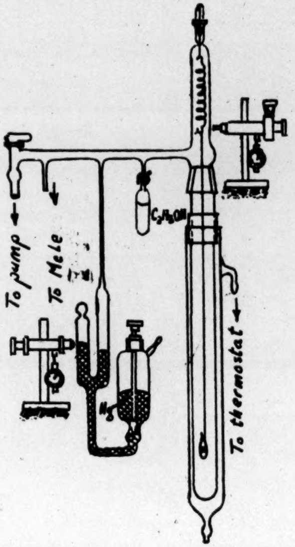

Fig. 2. Diagram of Sorption Balance.

The technique of sorption measurements is fairly simple. Prior to the experiment the whole apparatus, including the tube containing the sorbent, is carefully evacuated. Then, by turning the taps, the spaces V_1 and V_2 are disconnected, and into the first of these a certain amount of vapor is introduced. The mercury in the right limb is brought into contact with the platinum (when the neon lamp flashes) and the pressure of the vapor, P_1, is measured. The spaces V_1 and V_2 are then connected together by turning the tap, and a part of the vapor passes in to fill the tube V_2 and part is absorbed by the sorbent. The mercury is again brought to the contact, and the equilibrium pressure P_2 of the vapor is measured. From the gas laws we may calculate the loss of vapor due to absorption by the sorbent:

$$P_1V_1 = P_2(V_1 + V_2 + V_{\text{ads.}}). \qquad (1)$$

In spite of its simple construction, the apparatus gives results of high accuracy and reliability. This is achieved because of the following improvements: 1) absence of capillary communicating tubes; 2) reduction in the error due to inaccuracy of graduation (V_1 and V_2); 3) reduction of nonthermostated space to a minimum; 4) increase in accuracy of measurement of pressure owing to the use of an electric contact; 5) reduction of number of taps in the apparatus to a minimum.

The degree of accuracy attainable may be judged from the fact that we have obtained reproducible isotherms for the sorption of ethanol vapor by the walls of the empty tube. The apparatus is very convenient in use, and the time taken by an experiment is considerably shortened, owing to the following circumstances: 1) evacuation is rapid, owing to the shortness and width of the communicating tubes; 2) for the same reason sorption equilibrium is attained rapidly; 3) use of the plunger closing device enables raising and lowering of the mercury to be carried out rapidly.

Choice of Optimum Dimensions for the Spiral of a Sorption Balance

In the measurement of sorption by the gravimetric method a sorption balance is used, and one of the essential features of such a balance is a spiral of fine quartz thread. A diagram of a sorption balance is given in Fig. 2; it is unnecessary here to explain the purpose served by the various components. The accuracy of weighing depends on the choice of the dimensions of the spiral. The choice of these dimensions is generally made on the basis of "empirical considerations". We are not aware, however, of any experiments or calculations carried out for this purpose. It is an open question whether it is an advantage to use extremely fine quartz threads for making the spirals. The capacity of a balance constructed from very fine threads would be extremely low, and it would not be possible, therefore, to weight a sample of perceptible weight on such a balance.

It will be readily seen that the quality of a balance spiral is determined by the product of the capacity* and the sensitivity**; this quantity will also be a measure of the accuracy of weighing***. In order, therefore, to decide which of two spirals is the better (i.e. the more accurate), it is necessary to calculate the capacity and sensitivity in each case and then multiply these quantities together: the spiral for which this product is the greater will be the more accurate. If spiral A is twice as sensitive as spiral B, but the capacity of the first is half that of the second, then for weighing purposes, evidently, the two spirals will be equivalent, the only essential difference being that spiral A will be more prone to accidental breakage, being constructed from finer thread.

In the construction of spirals, it is necessary to make the number of turns as great as possible, for sensitivity can then be increased without reduction in capacity. The number of turns is generally limited by the length of the thread, which is often determined by the length of the sweep of the glass blower's arm. In practice it is not necessary to obtain very long threads: the individual spirals can be hooked together in a string.

It is shown in courses on the strength of materials [5] that the extension of a spiral is related to its dimensions by the equation:

$$\frac{\lambda}{P} = \frac{4R^3 n}{G r^4}, \tag{2}$$

where λ is the extension of the spiral (mm); P is the load (g); $\frac{\lambda}{P}$ is the sensitivity of the spiral (mm/g); R is the radius of a turn of the spiral; r is the radius of the thread; n is the number of turns (taken as 10 under the conditions of our problem; G is the shear modulus for quartz, which, according to our determinations, is $0.24 \cdot 10^7$ g/sq.mm. The maximum permissible load on the spiral, below which elongation is proportional to load, is related to the dimensions of the spiral by the equation:

$$P_{max} = \frac{\pi \sigma r^3}{2R}, \tag{3}$$

where P_{max} is the maximum permissible load (capacity) for the spiral (g), and σ is the permissible shearing load for quartz, which, according to our measurements, is $0.265 \cdot 10^4$ g/sq.mm.

The values of G and σ were found from three experiments with quartz spirals, mean values being taken. The value of G was found by substitution of the values of R, r, and n (obtained from measurements on the spirals) in Equation 2; the values of λ and P were taken from the calibration curves****. The value of σ was found by substitution of values of R and r in Equation 3. The value of P_{max} was again taken from the calibration curves.

By the use of Equations 2 and 3 we calculated the sensitivities and capacities of quartz spirals of various dimensions, the number of turns being ten in each case. The results are given in the table, in which at intersections of R-columns and r-rows the following figures are given:

Multiplicand — capacity of spiral (g)
Multiplier — sensitivity (mm/g)
Product — which is a measure of the accuracy of weighing

For example, a spiral for which the radius of a turn is R = 8 mm and the radius of the thread is r = 0.1 mm has a sensitivity of 85 mm/g and a capacity of 0.334 g, while the product of these quantities, which is a measure of the quality of the spiral, is 28.3 mm. It will be seen from the table that another spiral, for which R = 50 and r = 0.2, has a sensitivity of 1300 mm/g and a capacity of 0.668 g. In general, other things being equal, weighing with

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* Capacity is to be understood as the limiting load applied to the spiral beyond which the linear relation between elongation and load no longer applies.

** Sensitivity is to be understood as the elongation (mm) of the spiral produced by a load of 1 g.

*** Accuracy of weighing is to be understood as the ratio expressed as percent of the absolute error to the weight of the sample.

**** The calibration curves for the spirals, i.e. plots of $\lambda = f(P)$, are not given in the text.

TABLE 1

mm →	R = 6	R = 8	R = 10
↓	R^3 = 216	R^3 = 512	R^3 = 1000
r = 1	0.0036 X 250 = 0.9	0.0085 X 334 = 2.83	0.0166 X 416 = 6.9
r = 0.5	0.057 X 32.3 = 1.84	0.136 X 41.5 = 5.65	0.265 X 52.0 = 13.8
r = 0.2	2.25 X 2.0 = 4.5	5.33 X 2.67 = 14.3	10.4 X 3.34 = 34.6
r = 0.1	36 X 0.25 = 9.0	85 X 0.334 = 28.3	166 X 0.416 = 69.0
r = 0.05	572 X 0.0323 = 18.4	1360 X 0.0415 = 56.5	2650 X 0.052 = 138
r = 0.02	22,500 X 0.002 = 45.0	53,300 X 0.00267 = 143	104,000 X 0.00334 = 346

NOTE: The multiplicand is the capacity of the spiral (g); the multiplier is the sensitivity (mm/g).

$$P_{max} = \frac{\pi \sigma r^3}{2R} \quad ; \quad \frac{\lambda}{P} = \frac{4R^3 n}{G r^4}$$

$$G = 0.24 \cdot 10^7 \text{ g/sq. mm}; \quad \sigma = 0.265 \cdot 10^4 \text{ g/sq.mm}; \quad n = 10 \text{ turns}$$

the aid of the second spiral will give results that are 30.7 times as accurate as those obtained with the aid of the first.

An analytical investigation shows, therefore, that increase in the accuracy of weighing may be achieved not so much by reduction in the thickness of the thread, as by increase in the radius of a turn of the spiral. Finally, we have checked our calculations experimentally for glass spirals of various dimensions. This experimental test has fully confirmed the conclusion that for the purpose of weighing it is desirable to use fine spirals in which the radius of a turn of the spiral is high. The correct choice of the dimensions of the quartz spiral used in a balance may lead to a several-fold increase in the accuracy of weighing, a matter of considerable importance in the study of sorption processes.

SUMMARY

1. An apparatus is described for the measurement of sorption by the volumetric method. It is simple to construct and enables sorption measurements to be made with high accuracy.

2. The optimum dimensions of a quartz spiral for a sorption balance have been calculated. The calculations show that the accuracy of weighing can be increased not so much by reduction in the thickness of the thread, as by increase in the radius of a turn of the spiral.

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Table 1

R = 12	R = 14	R = 20	R = 50
$R^3 = 1728$	$R^3 = 2444$	$R^3 = 8000$	$R^3 = 125,000$
0.0284 X 346 = 9.8	0.0405 X 296 = 12	0.133 X 208 = 27.7	208 X 83.2 = 173
0.459 X 43.5 = 20	0.645 X 37 = 23.8	2.12 X 26 = 54.8	33.2 X 10.4 = 346
18.0 X 2.77 = 50	25.4 X 2.37 = 60	83 X 1.67 = 138	1300 X 0.668 = 870
284 X 0.346 = 98	405 X 0.296 = 120	1330 X 0.208 = 277	20,700 X 0.0832 = 1730
4590 X 0.0435 = 200	6450 X 0.037 = 238	21,200 X 0.026 = 548	332,000 X 0.0104 = 3460
180,000 X 0.00277 = 500	254,000 X 0.00237 = 600	830,000 X 0.00167 = 1380	13,000,000 X 0.000668 = 8700

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HYDROTECHNICAL CEMENTS IN THE CENTRAL ASIAN REPUBLICS*

I. S. Kantsepolsky

Resolutions carried at the Nineteenth Congress of the Party have set responsible and honorable tasks for scientific workers and for workers in the silicate industry.

For some years the silicate chemistry laboratory of the Institute of Chemistry, Uzbek Acad. Sciences, has studied local mineral raw material with the aim of producing water-stable and sulfate-stable cements. It is known that the ability of many binding materials to harden in water is based on the formation of sparingly soluble hydrosilicates and hydroaluminates of calcium. Among all the known binding substances, aluminous cement shows the greatest propensity to undergo hydraulic hardening. Portland cement occupies the second place. Present-day chemistry and technology permits the preparation of a cement having a strength approximating to that of a natural stone, such as marble; but when we bring about improvement in the mechanical strength of cement, its deficiencies become more and more pronounced, for they depend on the very essence of the hardening process. Cement consists essentially of : $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. As a result of detailed investigation of the hydration, hydrolysis, and hardening processes for individual clinker minerals and cements, it has been established that tricalcium silicate, the principal mineral present in cement clinker causing the hydraulic hardening of the cement, undergoes hydrolysis, under the action of the limited amount of water required for the formation of a plastic dough, with formation of a less basic hydrogel of calcium orthosilicate and with separation of free lime. Dicalcium silicate undergoes hydration very slowly and forms a hydrogel of calcium orthosilicate. Tricalcium aluminate undergoes hydration forming tetracalcium hydroaluminate.

The question of the hydrolysis and hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ remains an open one. Thus, of all the minerals present in cement clinker, only $3CaO \cdot SiO_2$ undergoes hydrolysis with separation of free lime. The content of $3CaO \cdot SiO_2$ in present-day cement may be as high as 70%. Hence in cement that has undergone prolonged hydration, much lime accumulates—up to 15%. The formation of a crystalline concretion of calcium hydroxide under conditions that preclude its dissolution constitutes a positive factor in the hardening of cement; but under the action of large amounts of water, as occurs in hydrotechnical construction, the lime is leached out, and the more rapidly this occurs, the less compact the concrete will be. The leaching of free lime leads to hydrolysis of the other products of the hardening of cement mortars and concretes. In fresh water, however, the disruption of hydrotechnical structures occurs only slowly, entirely owing to the formation of a protective film of calcium carbonate, which delays the diffusion of water through the outer surface; but it is not possible for the protective crust to prevent the leaching of lime completely, since its thickness, even after prolonged hardening, attains a value of only 5-10 mm.

In his classical work on hydraulic cements, Baikov [1] has shown that these cements can give stable systems under natural conditions only when an appreciable proportion of the lime present is able to be converted into carbonate before it is leached out in the free condition or bound in the form of silicates and aluminates. Baikov has concluded, therefore, that hydrotechnical structures of Portland cement are bound to be disrupted, owing to the leaching of the lime. Although in fresh waters, owing to the formation of a compact concrete (which is associated with the use of large amounts of cement), hydrotechnical structures made from Portland cement last for many decades, in mineralized sulfate waters the disruption process proceeds fairly rapidly. Sulfates act on tetracalcium hydroaluminate with formation of calcium sulfoaluminate. The crystals of calcium sulfoaluminate, formed by combination with the original solid phase of 3 molecules of gypsum and 31 molecules of water, occupy a considerably greater volume than $4CaO \cdot Al_2O_3 \cdot aq$. Stresses arise which lead to the disruption of the hydrated cement.

The theoretical concepts that we have outlined concerning the hardening of Portland cement are confirmed by its behavior in various media (see the figure). Cement hardens best in an atmosphere saturated with water vapor, for in this medium the best conditions obtain for the hydration of the cement. The increase in strength from 28 days to 2 years is 100% (Curve 2). In spite of the exceptionally severe conditions that we specially created for the hardening of cement in the air (the samples were transferred to the air after they had been hardened for only one day in a damp place), the samples showed a smooth rise in strength, whereas the samples kept in water showed no further rise after six months. In a 5% solution of Na_2SO_4 the cement had already lost 65% of its strength in six months, and after two years had become a formless mass (Curve 5). In a sulfate solution close in composition to the corrosive subsoil waters of Bukhara, the cement constantly lost in strength and was practically destroyed after two years. Thus, Portland cement, which is a very effective binding material for above-ground construction, cannot rationally be used in hydrotechnical construction and is completely unusable in mineralized sulfate waters.

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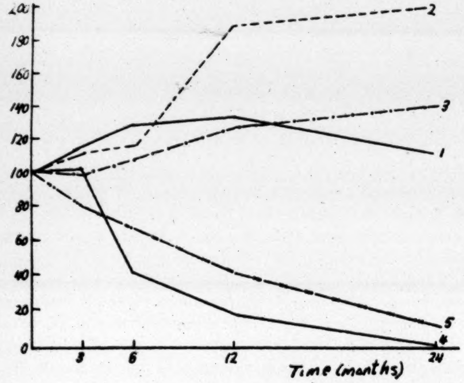
* Paper read at a conjoint session of the Division of Chemical Sciences of the USSR Academy of Sciences and the Academy of Sciences of the Uzbek SSR held on 25th of October, 1952 in Tashkent.



Change in the strength of Portland cement when hardened in different media (as a percentage of the strength of a 28-day-old cement): 1) in water; 2) damp atmosphere; 3) in air; 4) in a 5% Na_2SO_4 solution; 5) in Bukhara water.

In order to obtain high-grade water-stable and sulfate-stable cements, it is essential to follow the road laid down by the elder generation of Soviet scientists: Baikov [1], Druzhinin [2], Kind [3], Yung [4], and Budnikov [5]: free lime must be bound by active silica to give difficultly soluble calcium hydrosilicate. As numerous investigations have shown, the composition of calcium hydrosilicate depends on the pH of the solution, and, when sufficient active silica is present, calcium metasilicate is formed, which gives a limiting CaO concentration at 30° of 0.052 g per liter. The solubility of lime in presence of active silica is therefore reduced thirty-fold.

Hence, as Baikov has shown, the carbonation of lime in presence of sufficient active silica occurs before it can dissolve. Incidentally, it should be noted that Baikov's remarkable idea — that the hardening process in hydraulic cements constitutes, in effect, the formation of calcium carbonate — was first confirmed experimentally by Myakinchenko [6], a scientist of our laboratory, working with glinite cement. It was established that, everything considered, the hydraulic hardening of glinite cement did actually amount to the formation of calcium carbonate. In presence of a sufficient amount of active silica, sulfate attack on Portland cement is also eliminated. Although the introduction of hydro-additives does not prevent the formation of calcium sulfoaluminate, disruption of the hydrated cement does not occur in presence of sufficient amorphous silica. Yung [7] explains this by the deposition of the calcium sulfoaluminate, formed under these conditions through the liquid phase, in the pores of the cement, without disruption of its structure. This explanation often encounters great difficulties.

Numerous investigations in our laboratory have shown that the content of free lime in samples immersed in a sulfate medium may attain 7%. In presence of such a large amount of free lime, tetracalcium hydroaluminate cannot undergo hydrolysis. We consider that the mechanism of the formation of calcium sulfoaluminate in cement with hydro-additives is the same as that operating in cement without hydro-additives. The formation of calcium sulfoaluminate in these cements occurs through the solid phase by the direct combination of calcium sulfate with insoluble tetracalcium aluminate.

We explain the sulfate-stability of cement in presence of sufficient active silica by the favorable conditions for the crystallization of calcium sulfoaluminate in an elastic medium, rich in colloidal formations.

Thanks to extensive investigations by Soviet scientists, beginning from 1930 here in the Soviet Union, the production of a new hydrotechnical cement, called pozzolanic Portland cement, has been established. This hydrotechnical cement is obtained by the introduction of hydraulic additives to Portland cement clinker before grinding. The widest application has been obtained by pozzolanic Portland cements having additions of tripolite, which contains much active silica. The great experience gained in the mass production and varied application of this cement, and also the wealth of experimental material that has accumulated in research institutes, has enabled a clear picture of the value and defects of pozzolanic Portland cement to be formed. While having considerable advantages over Portland cement with respect to water-stability and sulfate-stability, pozzolanic cements have a number of defects. Pozzolanic cements, owing to the slow interaction of the active silica with lime and their high water demand, harden more slowly than Portland cements. Also, pozzolanic cements are less resistant than Portland cements to the alternate action of water and frost.

For this reason, the building material section of the committee set up by the Presidium of the USSR Academy of Sciences for coordination with the construction of hydro-stations, canals, and irrigation systems (chairman: Budnikov) has recommended the use of three types of cement for hydrotechnical concrete, according to the hardening conditions of the concrete or ferroconcrete in the structures. For concretes and ferroconcretes that are subjected to the systematic action of water and frost, it is recommended that a cement without hydro-additives and having a C_3A content of not greater than 5 % should be used. For the interior of massive concrete and ferroconcrete, pozzolanic Portland cement is recommended; the C_3A content of the original cement should not be greater than 7%. For concretes and ferroconcretes on the outer parts of structures, a cement having a C_3A content of up to 8% is recommended; up to 10% of hydro-additives is permissible. Such is the general position of the question of hydrotechnical cements.

In the Central Asian Republics there is a great need for sulfate-stable cements, which results from the high degree of mineralization of the subsoil waters in a number of districts. Having regard for the urgency of this question, the silicate chemistry laboratory, as already indicated, has for some years been making a study of local mineral raw materials with the object of preparing water-stable and sulfate-stable cements.

The most promising additives for the pozzolanization of Portland cement to be found in the Central Asian Republics are the natural burnt clays. These clays are now called by the name introduced by the geologist Tsybyshev: "gliezh". Gliezhes were formed as the result of subterranean coal fires and are found in all the districts of Central Asia in which coal deposits occur. The gliezhes of Kzyl-Ki have been studied in the greatest detail [8]. In their chemical and mineralogical composition, gliezhes are fairly homogeneous and consist of burnt kaolinite clays in which an appreciable amount of sand is incorporated. As the question of the use of glinite for the preparation of sulfate-stable cement had not been solved, we paid special attention to the question of the effect of gliezh on the sulfate-stability of cement.

As a result of these investigations the question of the effect of glinite on the sulfate-stability of cement, which has been in dispute for a long time, has been definitely settled. It has been shown that it is possible to prepare sulfate-stable cements from glinite by two methods [9]: the first method consists in the preparation of sulfate-stable cements by the introduction into Portland cement of glinite prepared by roasting kaolinite clays to give complete dehydration of the kaolinite (600-800°).

In this case, as a senior scientist of our laboratory, Tashpulatov, showed [10], a sulfate-stable pozzolanic Portland cement is obtained by using the usual proportions of cement and hydro-additive (60% cement + 40% glinite). Although Yung, our acknowledged specialist on cements, treats with skepticism the possibility of preparing sulfate-stable pozzolanic Portland cements from glinite [7], we consider that scientifically based facts will prevail and that the glinite Portland cement developed by Tashpulatov will find wide application in mineralized sulfate waters.

The second method, developed by the author in conjunction with Galkina and Myakinchenko, consists essentially in the introduction into Portland cement of glinite prepared by roasting kaolinite clays at the temperature of the transition of silica from the amorphous to the crystalline condition (900-1000°). This method, being the most readily applicable for gliezhes, has indeed been the basis for the manufacture of pozzolanic Portland cement in the cement works of the republic. The limiting amount of active silica in the gliezh is 3.5%. Gliezh having this active-silica content increases the sulfate-stability of the cement in proportion to the amount added. The best proportions of cement and gliezh from the point of view of sulfate-stability is 30% of Portland cement and 70% of gliezh, since only with such proportions is the whole of the lime separating during the hardening of the cement taken up by the gliezh.

Gliezh, by its ability to give lime the property of hardening in water, is to be considered as an active hydraulic additive that is inferior to Bryansk tripolite only in the degree in which these properties are shown. By the introduction of up to 30% of gliezh we appreciably improved the water-stability and sulfate-stability of cement.

Investigations over many years of the properties of gliezh and of gliezh Portland cement, experience in its

TABLE 1

Chemical and Mineralogical Compositions of Cements Obtained under Manufacturing Conditions

Name of Cement	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Other radicals	H_2O at 105°
Cement VF	21.40	4.30	6.00	0.27	64.62	1.68	0.40	0.65	0.20
Cement F	22.35	5.31	5.81	–	63.90	1.62	0.61	0.18	0.23
Cement A	21.62	5.24	4.48	0.27	65.75	1.59	0.72	0.68	0.12
Cement V	21.79	4.75	2.94	0.29	67.15	1.71	0.02	0.53	0.27

TABLE 2

Chemical Composition of Artificially Prepared Aggressive Waters

Composition of solution	Solution No. 1	Solution No. 2	Solution No. 3	Solution No. 4	Solution of 0.59% Na_2SO_4	Solution of 1.18% Na_2SO_4	Solution of 3% Na_2SO_4
Temporary hardness	30°	14°	–	–	–	–	–
pH	7	7	–	–	–	–	–
Free CO_2, mg/liter	127	43	–	–	–	–	–
HCO_3', mg/liter	660	305.0	–	–	–	–	–
$Ca^{\cdot\cdot}$, mg/liter	350	265.2	421	562	–	–	–
$Mg^{\cdot\cdot}$, mg/liter	600	132.4	746	837	–	–	–
Cl', mg/liter	1,920	1695.0	1,020	2,141	–	–	–
SO_4'', mg/liter	4,480	1382.4	5,489	7,462	4,000	8,000	20,282
$Na^{\cdot}$ (by difference), mg/liter	2,104	1318.3	1,388	2,738	1,916	3,833	9,718
Total ions, mg/liter	10,114	5098.3	9,064	13,740	5,916	11,833	30,000
$Ca(HCO_3)_2$ mg/liter	876	405	–	–	–	–	–
$CaSO_4$, mg/liter	455	561	1,431	1,910	–	–	–
$MgSO_4$, mg/liter	2,964	662	3,730	4,140	–	–	–
Na_2SO_4, mg/liter	2,655	675	2,222	4,160	5,916	11,833	30,000
NaCl, mg/liter	3,164	2795	1,681	3,530	–	–	–
Total salts	10,114	5098.3	9,064	13,740	–	–	–

mass production, and experience in its application in various constructional work have shown that gliezh is a valuable and reliable hydraulic additive. Owing to the use of gliezhes, the cement works of the republic produce every year tens of thousands of tons more high-quality cement.

The question of the manufacture of high-quality, water-stable, sulfate-stable, frost- and atmosphere-resisting, and low-temperature cements has taken on national economic significance. A number of research institutes in our country are working on this problem, and our laboratory also is trying to solve this nationally important problem. We have set ourselves the task of increasing the sulfate-stability of cement and of pozzolanic Portland cement by changing the mineralogical composition of cement clinker. With this in view, one of the scientists of our laboratory, Zhabitsky, has synthesized a number of cements from calcium carbonate, silica gel, silica, and ferric oxide, differing in their mineralogical compositions. The sulfate-stability was examined in accordance with the demands made by technical conditions for hydrotechnical concrete (GOST 4798-49).*

The method consisted essentially in establishing the limiting bending strength of samples of the cement investigated when hardened in aggressive solutions or in drinking water. As a quantitative characteristic of stability, the stability coefficient (SC_6) of the cement in the given medium was taken; SC_6 is the ratio of the mean limiting bending strength for prisms of the given cement after six-months' hardening in the aggressive solution to the mean limiting bending strength for prisms of the same cement after six-months' hardening in drinking water. The water under test (the medium) was regarded as aggressive to concrete made from the given cement if SC_6 was not less than 0.8. The samples to be examined for sulfate-stability were transferred, after a preliminary hardening for fourteen days in water, to a 3% solution of sodium sulfate, which is very characteristic in its aggressive action.

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* GOST = All-Union State Standard.

Table 1

Σ	Free CaO	Calculated mineralogical composition (%)						$\frac{SiO_2}{Al_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
		C_3S	C_2S	C_3A	C_4AF	C_3A + + C_4AF	KH		
99.52	0.28	62	15	2	18	20	0.92	2.02	0.73
100.01	0.08	44	31	4	18	22	0.84	2.01	0.91
100.47	0.15	55	23	7	14	21	0.89	2.16	1.23
99.45	0.22	70	9	8	9	17	0.95	2.74	1.68

TABLE 3

Analysis of Samples of Cement Hardened in 3% Na_2SO_4 Solution (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.49	17.96	11.06	6.90
"	2	0.85	20.53	13.27	7.26
"	3	Traces	26.52	18.13	8.39
"	6	"	29.37	21.28	8.09
Cement VF with 30% gliezh	1	1.18	13.77	7.48	6.29
"	2	0.33	13.79	6.39	7.40
"	3	0	17.42	10.64	6.78
Cement VF with 50% gliezh	1	0.37	9.87	3.43	6.44
"	2	Traces	9.99	3.01	6.98
"	3	0	9.78	3.40	6.38
"	6	0	9.53	4.52	5.01
Cement A	1	2.25	22.51	14.53	7.98
"	2	0.40	22.96	18.41	8.55
"	3	Traces	31.53	22.93	8.60
"	6	"	30.72	20.19	10.53
Cement A with 30% gliezh	1	0.46	13.39	6.92	6.47
"	2	Traces	14.53	6.68	7.85
"	3	"	15.93	8.59	7.34
"	6	"	15.75	8.46	7.29
Cement A with 50% gliezh	1	0.26	9.35	3.72	5.63
"	2	Traces	8.95	2.74	6.21
"	3	"	9.91	3.86	6.05
"	6	"	6.60	2.58	4.02
Cement V	1	3.05	19.00	9.15	9.85
"	2	1.37	27.45	13.48	13.97
"	3	1.23	28.00	16.48	11.52
"	6	0.24	30.46	20.25	10.21
Cement V with 50% gliezh	1	0.42	13.08	6.42	6.66
"	2	0.55	11.05	2.96	8.09
"	3	0.44	10.69	2.58	8.11
"	6	0.11	10.71	3.07	7.64
Pozzolanic Portland cement with tripolite	1	1.20	13.50	6.15	7.35
"	2	0.77	14.40	7.16	7.24
"	3	0.37	13.75	6.53	7.22
"	6	0.10	15.31	6.81	8.50

TABLE 4

Analysis of Samples of Cement Hardened in Aggressive Solution No. 1 (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.95	7.17	2.14	5.03
"	2	2.13	7.33	2.24	5.09
"	3	Traces	7.94	3.16	4.78
"	6	0	8.36	3.47	4.89
Cement VF with 30% gliezh	1	1.33	6.10	1.46	4.64
"	2	0.58	6.05	1.42	4.63
"	3	0.14	6.55	2.07	4.48
"	6	0	7.25	2.68	4.57
Cement VF with 50% gliezh	1	0.24	6.82	2.01	4.81
"	2	0	7.33	1.82	5.51
"	3	0	8.48	3.11	5.37
"	6	0	9.87	4.67	5.20
Cement A	1	3.45	9.92	4.06	5.86
"	2	—	12.56	5.54	7.02
"	3	1.26	12.51	5.90	6.61
"	6	—	13.81	6.83	6.98
Cement A with 30% gliezh	1	0.38	8.76	3.09	5.67
"	2	0.29	9.43	3.26	6.17
"	3	Traces	11.31	4.55	6.76
"	6	"	11.20	4.61	6.59
Cement A with 50% gliezh	1	0.11	6.7	1.34	5.42
"	2	Traces	7.07	1.54	5.53
"	3	0	9.16	3.50	5.66
"	6	0	8.13	2.14	5.99
Cement V	1	3.11	8.74	3.07	5.67
"	2	—	11.99	4.54	7.45
"	3	1.60	12.51	4.37	8.14
"	6	0.16	14.75	4.32	10.43
Cement V with 50% gliezh	1	—	8.00	2.92	5.08
"	2	—	9.35	3.01	6.34
"	3	0.37	9.95	3.42	6.53
"	6	Traces	10.95	4.09	6.86
Pozzolanic Portland cement with tripolite	1	0.65	8.18	2.85	5.33
"	2	Traces	9.33	3.33	6.00
"	3	"	8.90	3.20	5.70
"	6	0	11.59	4.52	7.07

The solution was changed every two months. The results of the investigations show that Portland cement without hydro-additives is disrupted by a 3% sodium sulfate solution: the stability coefficient is less than 0.8. Cements of high C_3A content are destroyed particularly rapidly. Pozzolanic Portland cements prepared from cement clinker having a C_3A content of up to 5% withstand the test (SC_6 is not less than 0.8). The results of the laboratory investigations were checked under manufacturing conditions at one of the Uzbekistan cement works. By the addition of ferric slag to the mix we obtained four batches of cement of varying mineralogical composition (Table 1). The cements produced under manufacturing conditions satisfied the technical requirements for high-quality cements. Pozzolanic Portland cements prepared from these cements and containing 30 and 50% of gliezh had compression strengths after a 28 day hardening in water of 300-400 kg/sq.cm for rammed mortars and 180-240 kg/sq.cm for plastic mortars. A study was made of the effects of additions of gliezh, Darbazin "opoka" (silica-containing clay), and Bryansk tripolite on the frost-resistance of the cement; the chemical composition is given in Table 1 under the designation F. Testing was carried out on plastic mortars (1:3 with Volsk sand). The temperature in the cold room was −14-24°.

TABLE 5

Analysis of Samples of Cement Hardened in Aggressive No. 2 (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.42	7.49	1.32	6.17
"	2	0.79	6.55	0.43	6.12
"	3	–	8.35	2.02	6.33
"	6	–	9.07	2.68	6.39
Cement VF with 30% gliezh	1	1.35	6.27	1.00	5.27
"	2	–	7.92	1.82	6.10
"	3	–	7.04	2.12	4.92
"	6	–	7.97	2.75	5.22
Cement VF with 50% gliezh	1	–	5.30	1.80	3.50
"	2	–	5.66	1.02	4.64
"	3	–	5.72	2.51	3.21
"	6	–	6.06	1.59	4.47
Cement A	1	–	7.39	2.17	5.22
"	2	–	8.21	1.75	6.46
"	3	–	7.88	2.04	5.85
"	6	–	12.45	4.61	7.84
Cement A with 30% gliezh	1	–	6.21	1.26	4.95
"	2	–	6.00	1.05	4.95
"	3	0.11	7.51	2.23	5.28
"	6	0	7.80	2.38	5.42
Cement A with 50% gliezh	1	–	5.90	1.52	4.38
"	2	–	5.70	0.78	4.92
"	3	–	–	–	–
"	6	–	5.66	1.53	4.13
Cement V	1	2.43	6.50	1.16	5.34
"	2	–	–	–	–
"	3	2.27	8.82	1.41	7.41
"	6	0	9.58	2.94	6.64
Cement V with 50% gliezh	1	–	–	–	–
"	2	–	5.98	2.58	3.40
"	3	0.38	7.19	0.98	6.21
"	6	–	–	–	–
Pozzolanic Portland cement with tripolite	1	1.43	4.59	0.93	3.66
"	2	–	–	–	–
"	3	0.72	6.37	0.97	5.40
"	6	–	6.88	1.37	5.51

Portland cement, with and without additions of 15% gliezh, showed great frost-resistance to 100 freezing cycles. Cements having additions of 15% opoka, 15% tripolite, and 30 and 50% gliezh lost from 10 to 27% in strength after 100 cycles (as compared with similar specimens hardened in wet sawdust). A notable deleterious effect on the frost-resistance was produced by Darbazin opoka. A cement containing 15% opoka was equivalent in frost-resistance to a pozzolanic Portland cement containing 50% gliezh. As in the determination of sulfate-stability in a 3% solution of Na_2SO_4 by the method given all the cements produced under laboratory conditions were broken down, irrespective of their C_3A content and basicity; in the determination of the sulfate-stability of cements produced under manufacturing conditions, we used, in addition to 3% Na_2SO_4, salt solutions that were close in composition to the subsoil waters of a number of Central Asian districts. Also, a high-alite cement – aluminoferrite cement VF – was tested in a saturated solution of calcium sulfate and in a Na_2SO_4 solution having SO_4'' content of up to 8000 mg/liter. The chemical compositions of the aggressive waters are given in Table 2.

TABLE 6

Sulfate-Stability of Cements Produced under Manufacturing Conditions. Pozzolanic Cements Prepared from them by Addition of Gliezh and Pozzolanic Cement

Name and composition of cement	Milling fineness (%)		Mixing water (%)	Limiting bending strength of a 1:3.5 mortar (kg/sq.cm)																								
	residue on 900 mesh per sq.cm sieve	passed 4900. mesh/sq. cm. sieve		in drinking water							in Solution No. 1						in Solution No. 2						in Na_2SO_4 solution					
				Duration (months)																								
				$\frac{1}{2}$	1	2	3	6	9	12	1	2	3	6	9	12	1	2	3	6	9	12	1	2	3	6	9	12
Cement VF	0.5	95.2	8.9	26	30	33	38	33	35	33	34	36	45	42	40	41	33	31	30	32	32	35	28	30	18	16	16*	19*
Cement VF with 30% gliezh	0.4	95.5	8.5	26	34	35	40	44	41	47	38	48	60	55	50	55	36	49	44	47	42	48	39	41	50	27	25	17
Cement VF with 50% gliezh	0.4	95.0	8.1	21	34	37	41	42	46	47	37	49	48	53	51	55	30	45	41	47	56	49	36	44	43	35	22	20
Cement A	0.5	95.9	9.6	25	34	36	38	42	42	41	34	32	33	32	36	36	34	28	26	25	33	36	20	25	22	18	16*	16*
Cement A with 30% gliezh	0.4	95.3	9.3	24	37	38	41	46	42	40	37	47	44	54	52	54	33	36	39	42	36	40	35	37	41	33	24	27
Cement A with 50% gliezh	0.4	94.9	8.2	20	30	33	34	38	39	36	37	42	41	48	48	47	31	36	41	42	40	38	32	40	51	19	25	17
Cement V	0.1	96.3	9.6	31	29	32	37	38	44	35	31	25	29	26	22	20	27	30	29	29	32	33	15	14	14	18*	21*	18*
Cement V with 50% gliezh	0.2	97.6	8.9	21	24	28	36	37	36	39	29	34	45	45	43	44	26	28	35	36	36	33	22	28	29	42	35	25
Pozzolanic Portland cement with Bryansk tripolite	0.4	93.9	10.7	22	27	29	31	41	45	40	36	35	46	48	48	49	29	35	33	35	37	34	36	32	36	43	36	31

TABLE 7

Sulfate-Stability of Cement VF with 50% Added Gliezh in Various Media

Name and composition of cement	Milling fineness (%)		Mixing water (%)	Limiting bending strength of a 1:3.5 mortar (kg/sq. cm)																				
	Residue on 900 mesh//sq. cm. sieve	Passed 4900 mesh//sq.cm sieve		In drinking water					In saturated $CaSO_4$ solu.				In solution No. 3				In solution No. 4				0.58% sol. of Na_2SO_4 **				1.18% sol. of Na_2SO_4 ***			
				Duration (months)																								
				$\frac{1}{2}$	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12
Cement VF	0,1	98	10	18	26	29	32	35	27	29	34	24	34	32	29	20	31	27	20	20	26	28	31	27	28	32	32	26
Cement VF with 50% gliezh	0.2	96	11.7	20	23	28	35	33	30	34	34	33	29	35	42	39	34	37	43	42	27	35	35	31	29	30	35	35

Parallel with the sulfate-stability determinations we made a study of the kinetics of the accumulation of calcium sulfate and sulfoaluminate during the hardening of cements in aggressive media. Determinations were made also of the amount of free lime in cements hardening in water and in aggressive media (Tables 3, 4, and 5).

If the kinetics of the formation of calcium sulfate and sulfoaluminate in cements hardening in a 3% solution of Na_2SO_4 are examined, the copious accumulation of calcium sulfate in the cements will be obvious. In spite of the large variation in mineralogical composition, the calcium sulfate contents of all the cement samples are practically identical and attain the value of about 30% in six months.

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* Asterisks against numbers indicate point at which cracks appeared in the samples.

** (4,000 mg SO_4'' per liter).

*** (8,000 mg SO_4'' per liter).

The process of calcium sulfate formation proceeds particularly vigorously during the early part of the period during which the cement is in the 3% Na_2SO_4 solution. Thus, already after one month the calcium sulfate content of the cements attains about 22%, which is 70% of the total amount of calcium sulfate formed in six months.

The kinetics of this process and the amount of calcium sulfate formed in the cements investigated might lead one to expect that they would have identical stabilities in a sodium sulfate solution. Their stabilities in this solution vary, however, and are directly related to the rate of calcium sulfoaluminate formation in the cement and to the total amount formed. Calcium sulfoaluminate is most rapidly formed in cement V, which is richest in tricalcium aluminate. The content of calcium sulfate bound as calcium sulfoaluminate after one month in 3% Na_2SO_4 attains 10%, and it reaches a maximum of 14% in two months, which corresponds to about 50% of the total amount of calcium sulfate that has accumulated in the cement. This cement (Table 6) loses 50% of its strength after only one month, and its stability coefficient SC_1 was only 0.52.

The content of calcium sulfate bound as calcium sulfoaluminate in cement VF, which has the least tricalcium aluminate content, is 7% at the end of one month, and attains a maximum of 8% after three months, which is only 27% of the total amount of calcium sulfate accumulating in the cement in six months. The strength of this cement after two months in 3% Na_2SO_4 is practically the same as that obtained in water. SC_1 and SC_2 are 0.93 and 0.91 respectively. An appreciable fall in strength occurs only in the third month: SC_3 is 0.47, and it remains at that level until the end of the six months.

Thus, in spite of accumulation of calcium sulfate in equal degree in the cements investigated, the rate of its conversion into calcium sulfoaluminate depends on the percent contents of tricalcium aluminate and tetracalcium aluminoferrite in the cements. Although the contents of silica and calcium sulfate are identical, the amount of calcium sulfoaluminate in cement V is almost double that in cement VF. It may, therefore, be considered to be established that even when there is a great accumulation of calcium sulfate in aluminoferrite cement the process of its conversion into hydrosulfoaluminate proceeds very slowly, which has a positive effect on its sulfate-stability.

The superiority of aluminoferrite cement over ordinary cement is very strikingly shown for hardening in sulfate solutions of low magnesium content having an $SO_4^=$ content of up to 4480 mg/liter. Calcium sulfate and sulfoaluminate formation during the first month of hardening in solution No. 1, occurs at the same rate for both cements, but later — from one to six months — the picture undergoes a great change Thus, in cement V the amount of calcium sulfate increases continuously and, at an age of six months, reaches 15%, of which 70% is in the form of sulfoaluminate; whereas in cement VF the calcium sulfate content attains 8.4% (against 7.2% at one month), including 5% of calcium sulfoaluminate, which comprises 60% of the total amount of calcium sulfate.

Thus, the hardening of cement containing 8% of tricalcium aluminate in sulfate solutions of low magnesium content is accompanied by continuous formation of calcium sulfoaluminate. In samples that have been hardened for six months the amount of sulfoaluminate attains 30%. Such a large amount of calcium sulfoaluminate is bound to lead to the disruption of the cement, which is indeed what we observe. Fall in strength begins already after two months in solution No. 1, and at six months SC_6 is 0.68.

In the aluminoferrite cement VF the process of forming calcium sulfoaluminate in a sodium sulfate solution of low magnesium content occurs only in the early period, mainly as a result of the tricalcium aluminate contained in this cement. This cement does not sustain any aggressive attack in six months in sulfate media of low magnesium content having an $SO_4^=$ content of up to 5000 mg/liter, and in pure calcium sulfate solutions it is stable at an $SO_4^=$ content of 8000 mg/liter (Table 7). According to the standards for water-aggressiveness, media for hydrotechnical concrete (GOST 4796-41) having an $SO_4^=$ content of higher than 4000 mg/liter are considered to be aggressive not only for Portland cement, but also for pozzolanic Portland cements. We may therefore consider it to be established that the aluminoferrite cement that we prepared under manufacturing conditions meets all the requirements of the standard specification mentioned for a sulfate-stable cement.

Finally, we will consider the kinetics of the accumulation of calcium sulfate and sulfoaluminate in pozzolanic Portland cements. The accumulation of calcium sulfate and sulfoaluminate in pozzolanic Portland cements having enough hydro-additive occurs only in the early part of the hardening period in the aggressive solution (3 % Na_2SO_4), coming almost to a standstill in one month. After this period the total calcium sulfate content of pozzolanic cements is 10-15%, including 6-8% as calcium sulfoaluminate.

It should be noted that more sulfate accumulates in pozzolanic Portland cement containing tripolite than in pozzolanic cement containing 50% gliezh; the maximum sulfate content, 13%, is attained after a one-month hardening in 3% Na_2SO_4. As time goes on, not only does no further accumulation of calcium sulfate occur, but, on the contrary, it is even lost to some extent owing to leaching. Pozzolanic Portland cements, therefore, unlike Portland cement, should have high stability to sodium sulfate solutions, and this is actually observed. Thus, it will be seen from an examination of the results of tests on cements in 3% Na_2SO_4 that pozzolanic cements prepared from cements V and VF acquire the sulfate-stability required under technical conditions by the addition of 50% of gliezh. A pozzolanic cement prepared from cement A acquires the required sulfate-stability only when 60% of gliezh is present.

In artificially prepared solutions of low magnesium content and having an SO_4'' content of up to 5000 mg/liter, the process of calcium sulfate/sulfoaluminate accumulation in pozzolanic Portland cements again occurs essentially in the early part of the hardening period. In pozzolanic cements, irrespective of the mineralogical composition of the cement clinker, the greater part of the calcium sulfate that accumulates occurs in the bound condition as calcium sulfoaluminate. The maximum amount of calcium sulfate present as sulfoaluminate is 8%, including 3% that is bound as sulfoaluminate already in the setting of the cement (because of the calcium sulfate introduced to control the setting time). Thus, owing to the interaction of free lime with sodium sulfate, only a further 5% of bound $CaSO_4$ is formed (as sulfoaluminate). Such an amount of calcium sulfoaluminate in pozzolanic Portland cement cannot have a deleterious effect on the stability of salt solutions of low magnesium content. Hence, all of the pozzolanic cements studied, not only with 50%, but also with 30% of gliezh, harden in salt solutions of low magnesium content (close in composition to the subsoil waters of a number of Central Asian districts) in the same way as in water.

The main results of the investigations may be summarized as follows:

1. A cement containing up to 5% of tricalcium aluminate and a total content of mineral fluxes of up to 22%, even with a saturation coefficient of 0.92, is stable in sulfate solutions of low magnesium content (containing up to 3000 mg/liter of magnesium sulfate) and having an SO_4'' content of up to 5000 mg/liter. The formation of calcium sulfate and sulfoaluminate occurs only in the early part of the hardening period and practically ceases by the end of one month.

2. Addition of gliezh to cement of low tricalcium aluminate content (up to 5%) has an exceptionally favorable effect on its sulfate-stability. Its favorable effect is already appreciable when a 15% amount of gliezh is added. Such a cement, containing 15% of gliezh, is not attacked in sulfate solutions of low magnesium content having an SO_4'' content of up to 7000 mg/liter.

3. A pozzolanic cement containing 30% of gliezh, prepared from a Portland cement having a tricalcium aluminate content of up to 8% and a total content of mineral fluxes of up to 20%, hardens in sulfate solutions close in composition to the aggressive subsoil waters of Central Asia in the same way as in fresh water.

4. Pozzolanic cement containing 50% of gliezh and prepared from a Portland cement having a tricalcium aluminate content of up to 5% and a total content of mineral fluxes of up to 21% with a saturation coefficient of 0.80 - 0.92 is stable in 3% solution of sodium sulfate: the stability coefficient, SC_6, is not less than 0.80. Formation of calcium sulfate and sulfoaluminate is to be observed only in the early part of the hardening period (up to one month). As time goes on this process dies down.

In this way we have shown that it is possible to manufacture in one of the cement works of the Republic a whole series of special cements that satisfy the requirements of the constructors of the Main Turkmen Canal for use in different zones of the canal.

Local loess-like clayey soils are of considerable interest for the preparation of hydrotechnical cements in the Central Asian Republics. We have shown [11] that these loess-like soils, when roasted in the range 650-750° acquire the properties of hydraulic binding materials. The hydraulic binding properties are caused by the formation, during the roasting, of calcium monoaluminate and β-orthosilicate. The cement so obtained is called "loess cement". The hardening of this cement proceeds with formation of a hydrogel of calcium monosilicate and dicalcium hydroaluminate. It is considerably better in strength than the best types of Roman cement. Loess cement hardens better in sulfate solutions than in fresh water. The low stability of loess cement to the atmosphere, which is the result of the deleterious action of atmospheric carbon dioxide, is completely eliminated by additions of silicate cement.

As a result of laboratory and factory (pilot and full-scale) investigations [12], it has been found possible to prepare loess cements of three grades, varying in mechanical strength:

1. Grade "250", with 50% of Portland cement
2. Grade "200", with 30% of Portland cement
3. Grade "100", with 10% of Portland cement

Cements of grades "200" and "250" may be used in the same way as pozzolanic cements in concrete and ferroconcrete for hydrotechnical construction, the loess cement with 10% of Portland cement being for mortars. Loess cement with 50% of Portland cement has been approved for hydrotechnical construction and is to be recommended as a high-quality hydrotechnical cement.

Among the important questions of cement chemistry and technology that have not yet been solved and yet are of great practical significance is the question of the aggressive action of magnesium-containing waters. In sulfate solutions of low magnesium content, (up to 1% magnesium sulfate) sulfate-stable pozzolanic cements do not suffer aggressive attack, but in solutions of higher concentration they are broken down even more rapidly than Portland cements. The question of the preparation of cements stable to magnesium sulfate solutions of high concentration is therefore a very vital one.

In view of this, an investigation of a senior scientist of our laboratory, Ragozina, is of great interest. In a study of the hardening processes in salt solutions of synthetic cements consisting of various proportions of calcium monoaluminate and calcium orthosilicate, Ragozina showed that they are extremely resistant to the aggressive action of sulfate- and magnesium-containing waters. Pursuing these investigations, Ragozina obtained a siliceous belite cement. This cement in admixture with 15% of anhydrite, which has a strength in plastic mortars of 200 kg/sq. cm., has a high degree of stability in a 3% solution of magnesium sulfate.

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*NKPS = Peoples Commissariat of Railroads.

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OPTICALLY ACTIVE ORGANOMERCURY COMPOUNDS

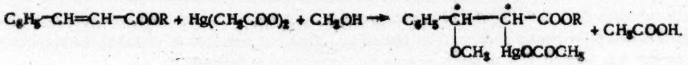
COMMUNICATION 1. PREPARATION OF THE DIASTERIOISOMERIC (l)-MENTHYL ESTERS OF (BROMOMERCURI)PHENYLACETIC ACID

A. N. Nesmeyanov, O. A. Reutov, and S. S. Poddubnaya

Optically active organometallic compounds containing a metal atom linked to an asymmetric carbon atom have received very little study. Only investigations on the preparation of optically active organometallic compounds of alkali metals, magnesium, and mercury have appeared in the literature. In spite of numerous attempts [1-7], optically active organometallic compounds of the alkali metals have only recently been prepared. Letsinger [8] in 1950, was successful in preparing 1-methylheptyllithium, the optical activity of which he inferred from an examination of its carbonation product.

Attempts to prepare optically active organomagnesium compounds have not been successful [9-11]: the work of Whitmore and Harriman [12] on the preparation of an optically active organomagnesium compound from 1-bromo-2-methylbutane in which the magnesium was attached to the carbon atom adjacent to the asymmetric carbon must be regarded with some doubt, as the experimental results are not sufficiently decisive.

Optically active organomercury compounds have been prepared by Marvel and coworkers by the addition of mercuric acetate to the menthyl [13] and bornyl [14] esters of cinnamic acid:

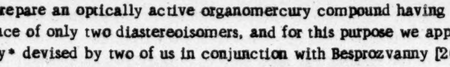


$$C_6H_5{-}CH{=}CH{-}COOR + Hg(CH_3COO)_2 + CH_3OH \rightarrow C_6H_5{-}\underset{OCH_3}{\underset{|}{\dot{C}H}}{-}\underset{HgOCOCH_3}{\underset{|}{\dot{C}H}}{-}COOR + CH_3COOH.$$

The acetate was converted into the chloride, bromide, or iodide by the action of potassium chloride, bromide, or iodide, and then separation of the diastereoisomers was carried out. In all cases only two diastereoisomers were obtained instead of the four that are theoretically possible, a circumstance that led Pfeiffer [15] to doubt the correctness of the formulas given above for the products of the addition of mercuric acetate to cinnamic esters and to suggest that these addition products are complex compounds. In view of the results of one of us with coworkers [16-19] concerning the structure of the products of addition of heavy-metal halides to acetylene and ethylene and the causes of their dual reactivity, it can now scarcely be doubted that the products of addition of mercuric acetate to cinnamic esters are true organometallic compounds.

In this connection, two suppositions are possible. First, we may suppose that Sandborn and Marvel failed to separate all of the four diastereoisomers. Second, we may suppose that in the addition of mercuric acetate to cinnamic esters only two of the four possible diastereoisomers are actually formed owing to the existence of stereochemically directed addition of mercury salts at a carbon-carbon double bond (trans addition).

We decided to prepare an optically active organomercury compound having a structure that would permit the possibility of existence of only two diastereoisomers, and for this purpose we applied the reaction of bromo derivatives with mercury* devised by two of us in conjunction with Besprozvanny [20]: (l)-menthyl bromo(phenyl) acetate reacted on being shaken vigorously with mercury, yielding an optically active organomercury compound:



$$C_6H_5{-}\underset{Br}{\underset{|}{\dot{C}H}}{-}COOC_{10}H_{19} + Hg \rightarrow C_6H_5{-}\underset{HgBr}{\underset{|}{\dot{C}H}}{-}COOC_{10}H_{19}.$$

We carried out this reaction for the two stereoisomeric menthyl esters of bromo(phenyl)acetic acid. The following constants are given in the literature [21] for the two stereoisomers: stereoisomer I - m.p. 78-79°, $[\alpha]_D$ +9.4°; stereoisomer II - m.p. 40-41°, $[\alpha]_D$ -139.8°. The constants that we obtained for isomer I agreed with the figures in the literature, but, in spite of the fact that we performed the synthesis of menthyl bromo(phenyl)acetate not less than fifteen times by two different routes, we never succeeded in obtaining isomer II in a crystalline form, neither by allowing the substance to stand for a long period (two months), nor by attempting to recrystallize it from various solvents. The specific rotation of the isomer II that we obtained was $[\alpha]_D^{18} = -98.5°$.

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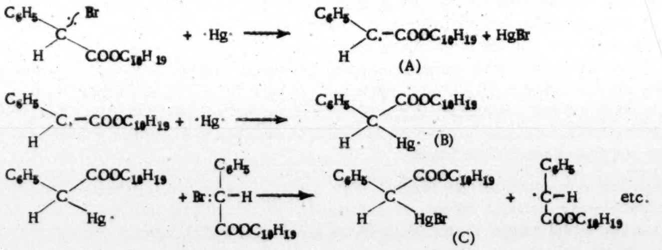
* Other methods for the synthesis of organomercury compounds (with the aid of the Grignard reagent, by the action of sodium amalgam on halogen derivatives, etc.), are not applicable here because they do not permit the preparation of organomercury compounds containing active groups, without which it is not possible to separate the stereoisomers.

The two stereoisomers reacted with mercury at different rates. Thus, the reaction of isomer II with excess of mercury proceeded in the cold under vigorous shaking for 30-60 minutes, giving 29% of the theoretical yield. The solid isomer I, however, when shaken in benzene solution with mercury in the cold for 250 hours gave only a 2.4% yield of organomercury compound. This very slow reaction is evidently associated with the reduction in the concentration of the menthyl ester; apart from this, the best solvent for the reactions of halogen derivatives of aliphatic or aryl-substituted aliphatic compounds with mercury is generally ethanol (and not benzene), which cannot be used in the present case owing to the poor alcohol-solubility of the solid menthyl ester. The differing rates of reaction must depend, of course, to some extent on the fact that the two isomers are not enantiomorphs, but diastereoisomers, and therefore will in general have differing reactivities If the reaction of the solid isomer of menthyl bromo(phenyl)acetate with mercury is carried out at 95-100° without solvent, reaction is complete in four hours and leads to the formation of the organomercury compound in 36% yield.

When mercury reacted with either the liquid or the solid isomer of menthyl bromo(phenyl)acetate, a mixture of two diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid was formed. The organomercury diastereoisomers were separated by fractional crystallization from methanol or acetone. The constants of the compounds obtained were: diastereoisomer I - m.p. 162-163°, $[\alpha]_D^{18} - 96.5° \pm 1°$; diastereoisomer II - m.p. 152-154°, $[\alpha]_D^{18} - 49.3° \pm 1°$.

It must be noted that when either the liquid* or the solid isomer of menthyl bromo(phenyl)acetate reacts with mercury, an equimolecular mixture of organomercury diastereoisomers is formed (angles of rotation of the mixtures of diastereoisomers formed in various cases were −71.1°, −73.8°, and −75.7°, and the calculated angle of rotation of an equimolecular mixture of diastereoisomers is $(-\frac{96.5+49.3°}{2} = -72.9° \pm 1°)$. This fact indicates that a free radical with an odd electron on carbon does not preserve the configuration of the compound from which it is formed, but becomes flat.**

As has been shown [20], the reaction of mercury with alkyl halide is homolytic, and is accelerated by addition of organic peroxides and by exposure to ultraviolet radiation. Thus, the reaction of menthyl bromo(phenyl)acetate (whether it be isomer I or isomer II) with mercury may be represented as follows:



The first stage consists in homolytic rupture of the C—Br bond owing to the attack of a mercury atom (or under the action of light) with formation of a free radical.

If the unpaired electron of the free radical were able to maintain the configuration, then one of the organomercury diastereoisomers would form, if not the sole, then the predominating product. Since it is found in practice that each of the isomeric menthyl bromo(phenyl)acetates forms an equimolecular mixture of organomercury diastereoisomers, it is obvious that the radical A has a flat configuration, as a result of which the attack on it by a mercury atom may occur, with equal probability, from either side.

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* The fact that the liquid isomer of menthyl bromo(phenyl)acetate may have contained some of its diastereoisomer is of no significance in our method of working.

** Contradictory hypotheses on this matter appear in the literature: thus, Wallis, and Adams [22] and also Brown, Kharasch, and Chao [23] consider that a free radical has a flat configuration, whereas Karagunis and Drikos [24] consider that the odd electron of the free radical is able to maintain the configuration.

EXPERIMENTAL

1. Preparation of the Diastereoisomeric (1)-Menthyl Esters of Bromo(phenyl)acetic Acid.

The menthyl ester of racemic bromo(phenyl)acetic acid was obtained in 68.5 % yield by the esterification of bromo(phenyl)acetic acid with (1)-menthol in presence of hydrogen chloride [21]. On standing, the substance partly crystallized out. After one week the precipitate was filtered off and recrystallized twice from methanol: m.p. 80°; $[\alpha]^{18}_D$ + 10.9° ± 0.3° (in alcohol) (C = 2.333*; $\underline{1} = 2$; α^{18}_D + 0.66° ±0.02°); data in the literature: 78-79°; $[\alpha]_D$ + 9.4° (in alcohol) [21].

Found %: C 61.30; 61.32: H 7.24; 7.28

$C_{18}H_{25}O_2Br$. Calculated %: C 61.19; H 7.13

The isomer II was obtained in the form of a thick liquid. The substance did not crystallize out when allowed to stand for two months; it did not crystallize also from aqueous alcohol, heptane, benzene, ether, and other solvents: b.p. 223-225°/22 mm; $[\alpha]^{18}_D$ −98.5° (in alcohol); (C = 0.739; $\underline{1} = 2$; α^{18}_D −1.13°). Data in the literature: 40-41°; $[\alpha]^{18}_D$ −139.8° [21]; 225°/22 mm [25].

2. Reaction of the (1)-Menthyl Esters of (d)- and (1)-Bromo(phenyl)acetic Acids with Mercury.

a) Reaction of the liquid isomer of (1)-menthyl bromo(phenyl)-acetate with mercury. A mixture of 149 g (0.42 mole) of the (1)-menthyl ester of bromo(phenyl)acetic acid having $[\alpha]^{18}_D$ −98.5° and 1177 g (5.86 g-atom) of mercury was shaken vigorously until it thickened (30 minutes). A day later the thick reaction mixture was washed with 96% alcohol, and the organomercury compound was extracted from the residue with acetone. After evaporation of the acetone, crude (1)-menthyl (bromomercuri)phenylacetate (68 g, 29.2%) was obtained. The angle of rotation of the uncrystallized substance (washed with cyclopentane) was: $[\alpha]^{18}_D$ −71.1°** (C = 0.777; $\underline{1} = 2$; α^{18}_D −0.98°). After recrystallization from alcohol it had an m.p. 158-161°; $[\alpha]^{18}_D$ −74.6° (C= 2.037; $\underline{1} = 2$; α^{18}_D −2.67°).

Found %: C 39.02; 39.14; H 4.59; 4.55

$C_{18}H_{25}O_2HgBr$. Calculated %: C 39.03; H 4.55

The (1)-menthyl (bromomercuri)phenylacetate obtained dissolved readily in chloroform and acetone, not so readily in benzene and toluene, and poorly in ether. It could be crystallized from ethanol, methanol, carbon tetrachloride, benzene, and acetone The substance is here described for the first time.

After recrystallization from various solvents, the substance gave various values of specific rotation. Thus, from acetone: $[\alpha]^{18}_D$ −91 2° (C = 0.731; $\underline{1} = 2$; α^{18}_D −1 17°); from carbon tetrachloride: $[\alpha]^{18}_D$ −64° (C = 0.95; $\underline{1} = 2$; α^{18}_D −1.07°); and from benzene: $[\alpha]^{18}_D$ −75.2° (C = 0.643; $\underline{1} = 2$; α^{18}_D −0.85°).

The great extent to which the angle of rotation depends on the nature of the solvent from which the substance is crystallized gives us reason to suppose that the substance is a mixture of two diastereoisomers of differing solubility and rotatory power.

b) Reaction of the solid isomer of (1)-menthyl bromo(phenyl)-acetate with mercury in benzene. A mixture of 35 g (0.09 mole) of the menthyl ester of bromo(phenyl)acetic acid having m.p. 80° and specific rotation $[\alpha]^{18}_D$ +10.9° dissolved in benzene, and 88 g (0.44 g-atom) of mercury was shaken for about 250 hours. The benzene was evaporated off, and the residue was washed with alcohol and extracted with hot acetone. The organomercury compound and unchanged menthyl bromo(phenyl)acetate went into the acetone. The acetone was evaporated off, and the organomercury compound was washed free of starting material by means of ether. The product was menthyl (bromomercuri)phenylacetate (1.3 g, 2.4 %) of m.p. 155-156°. After recrystallization from methanol it melted at 157-158°. A mixed melting point with authentic menthyl (bromomercuri)phenylacetate (m.p. 157-158°; $[\alpha]^{18}_D$ −75.8° showed no depression. The specific rotation was $[\alpha]^{18}_D$ − 73.8° (C = 0.783; $\underline{1} = 2$; α^{18}_D −1.02°).

c) Reaction of the solid isomer of the menthyl ester of bromo(phenyl)acetic acid with mercury at 95-100°. A mixture of 79 g (0.22 mole) of the menthyl ester of bromo(phenyl)acetic acid (m.p. 79-80°; $[\alpha]^{18}_D$ + 11.2°) and 235 g (0.86g-atom) of mercury was heated for four hours at 95-100° with vigorous shaking. Toward the end of this period, the original liquid reaction mixture began to become solid. After one day the mixture was washed with ether to remove unchanged starting material, and the organomercury compound formed was extracted with chloroform. Evaporation of the chloroform yielded a residue of menthyl (bromomercuri)phenylacetate (44.5 g, 35.9%), which melted, after being recrystallized from methanol, at 155-157°. It had $[\alpha]_D^{18} -75.7°$ (C = 0.764; l = 2; $\alpha_D^{18} -1.02°$).

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* The concentration $\underline{C}$ is always expressed in grams of substance per 100 g of solvent.

** Here and elsewhere the specific rotation is measured in benzene.

3. Separation of the Diastereoisomeric (l)-Menthyl Esters of (d)- and (l)-(Bromomercuri)phenylacetic Acids.

The separation of these substances was carried out by repeated recrystallization. Attempts to use benzene and carbon tetrachloride as solvents were not successful. After the substance had been recrystallized three times from benzene, it became dark in color owing to partial decomposition with separation of mercury. When it was recrystallized from carbon tetrachloride, its angle of rotation changed to an inappreciable extent. Thus after three recrystallizations $[\alpha]_D^{18}$ was $-73.8°$, and after four it was $-78.5°$: for complete separation of the diasteroisomers, several more recrystallizations would have been necessary.

It was found possible to effect the complete separation of the diastereoisomers by recrystallization from a large amount of methanol (6 g of menthyl [bromomercuri]phenylacetate from 200 ml of methanol). The first recrystallization yielded a substance of m.p. 159-160° and $[\alpha]_D^{18} -89.7°$ (C = 0.656; l = 2; $\alpha_D^{18} -1.03°$). A second recrystallization yielded 2.5 g of substance of m.p. 162-163° and $[\alpha]_D^{18} -96.7°$ (C = 0.658; l = 2; $\alpha_D^{18} -1.12°$).

Further recrystallization produced no further change in angle of rotation and melting point. Thus, after the third recrystallization the substance had an m.p. 162-163° and $[\alpha]_D^{18} -96.4° \pm 1°$ (C = 0.635; l = 2; $\alpha_D^{18} -1.10° \pm 0.01°$). The substance is described for the first time.

Found %: C 39.18; 39.19; H 4.55; 4.74
$C_{18}H_{25}O_2HgBr$. Calculated %: C 39.03; H 4.78.

The readily soluble isomer II of the menthyl ester of (bromomercuri)phenylacetic acid was separated from the filtrate from the first crystallization, which was evaporated to dryness. The residue was fractionally crystallized from methanol. For this purpose it was dissolved in the least possible amount of boiling methanol, and when the solution was cooled a precipitate formed (Fraction I) of m.p. 159-160° and $[\alpha]_D^{18} -85.5°$ (C = 0.666; l = 2; $\alpha_D^{18} -1.00°$). Each of the following fractions was a precipitate formed by evaporation of the filtrate to half volume. The angle of rotation of Fraction III was $[\alpha]_D^{18} -52.5°$ (C = 0.703; l = 2; $\alpha_D^{18} -0.65°$); and that of Fraction IV: $[\alpha]_D^{18} -50.9° \pm 1$ (C = 0.483; l = 2; $\alpha_D^{18} -0.43 \pm 0.01°$). There was no further change in the angle of rotation: thus Fraction V had $[\alpha]_D^{18} -49.3° \pm 1°$ (C = 0.671; l = 2; $\alpha_D^{18} -0.57° \pm 0.01°$); m.p. 152-154°. The substance is described for the first time.

Found %: C 39.31; 39.35; H 4.75; 4.74
$C_{18}H_{25}O_2HgBr$. Calculated %: C 39.03; H 4.55

The separation of the diastereoisomers can be effected also by recrystallization from acetone. After two recrystallizations from acetone, a substance was obtained having m.p. 160-161° and $[\alpha]_D^{18} -92.4°$ (C = 0.695; l = 2; $\alpha_D^{18} -1.13°$). After three recrystallizations from acetone the substance had an m.p. 162-163° and $[\alpha]_D^{18} - 95.9 \pm 1°$ (C = 0.725; l = 2; $\alpha_D^{18} -1.36° \pm 0.01°$).

SUMMARY

1. When the stereoisomeric (l)-menthyl esters of bromo(phenyl)acetic acid react with mercury, an equimolecular mixture of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid is formed in each case.

2. The fact of the formation of an equimolecular mixture of the diastereoisomers of (l)-menthyl (bromomercuri)phenylacetate is an argument in favor of the hypothesis that a free radical having an unpaired electron on a carbon atom has a plane configuration.

3. The two diastereoisomers of the (l)-menthyl ester of (bromomercuri)phenylacetic acid have been obtained in a pure state by fractional crystallization of their mixture from methanol or acetone.

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SYNTHESIS OF ORGANOMERCURY COMPOUNDS BY REACTION OF ORGANIC HALOGEN COMPOUNDS WITH MERCURY

O. A. Reutov and A. N. Nesmeyanov

In the literature a few examples have been described of reactions of organic iodine compounds with mercury in which organomercury compounds are formed These include the reactions of methyl iodide [1], ethyl iodide [2], allyl iodide [3], propargyl iodide [4], iodo(phenyl)acetylene [5], diiodomethane, iodoform [6], and benzyl iodide [7] with mercury. It has been considered that chlorine and bromine compounds of the aliphatic and aryl-substituted aliphatic series (with the exception of bromobenzyl cyanide [8]), and also all aryl halides, do not react with mercury.

In the present and previous [9] papers it is shown that bromine compounds in which the carbon-bromine bond is activated by conjugation with a double bond ($>C=\overset{|}{C}-\underset{|}{\overset{|}{C}}-Br$ or $O=\overset{|}{C}-\underset{|}{\overset{|}{C}}-Br$), are able to react with mercury to give organomercury compounds of the type $R-HgBr$; aromatic iodine derivatives are able to react with mercury to give organomercury compounds only in presence of ultraviolet radiation.

Allyl bromide reacted slowly with mercury in the dark, forming allylmercury bromide:

$$CH_2=CH-CH_2Br + Hg \rightarrow CH_2=CH-CH_2HgBr.$$

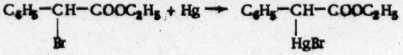
It was found that the reaction is accelerated by irradiation of the reaction mixture by means of a quartz mercury lamp contained in a glass vessel, and is further accelerated when the glass vessel is replaced by a quartz one, which transmits ultraviolet rays; in the latter case, vigorous stirring* is necessary, since otherwise organomercury polymers form rapidly on the walls of the quartz vessel. The results obtained for reactions of allyl bromide with excess of mercury under various conditions are given in Table 1.

Cinnamyl bromide reacted rapidly with mercury without irradiation, forming cinnamylmercury bromide in 82% yield:

$$C_6H_5-CH=CH-CH_2Br + Hg \rightarrow C_6H_5-CH=CH-CH_2-HgBr.$$

This reaction goes so vigorously that the cinnamyl bromide must be diluted with ethanol in order to obviate its polymerization and resinification.

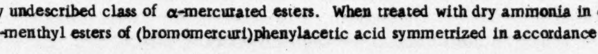
Ethyl bromo(phenyl)acetate readily reacted with mercury without irradiation, giving ethyl (bromomercuri)phenylacetate in 73% yield:



$$C_6H_5-\underset{\substack{|\\ Br}}{CH}-COOC_2H_5 + Hg \rightarrow C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOC_2H_5$$

The (l)-menthyl ester of bromo(phenyl)acetic acid reacted in like manner.

We considered it to be of interest to study some of the properties of the representatives that we had prepared of this previously undescribed class of α-mercurated esters. When treated with dry ammonia in chloroform solution, the ethyl and (l)-menthyl esters of (bromomercuri)phenylacetic acid symmetrized in accordance with the equation:



$$C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOR + 2NH_3 \rightarrow ROOC-\underset{\substack{|\\ C_6H_5}}{CH}-Hg-\underset{\substack{|\\ C_6H_5}}{CH}-COOR + NH_4HgBr + NH_4Br.$$

We studied also the reaction of a (bromomercuri)phenylacetic ester with acetyl chloride in a medium of dry

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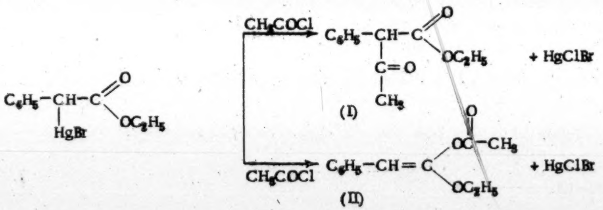
* We found the most suitable stirrer to be a rapidly rotating bottle brush. An improvised stirrer of this type produces a good emulsion of the mercury in the halogen compound and constantly removes the film of solid reaction products that forms on the wall of the test tube and would otherwise impede irradiation of the reaction mixture .

TABLE 1

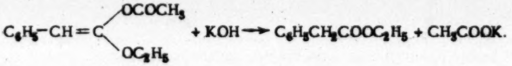
Reaction of Allyl Bromide with Mercury

No.	Source of irradiation	Reaction vessel	Agitation	Amt. of allyl bromide(g)	Duration of reaction (hr.)	Yield (%)	Notes
1	Lamp PRK-4	Quartz test tube	Vibratory machine	10	48	9	Apart from $CH_2=CHCH_2HgBr$, 1.5 times as much organomercury polymer was formed.
2	Lamp PRK-4	Glass test tube	Vibratory machine	11	48	20	Forms pure allylmercury bromide without appreciable contamination with polymeric compounds.
3	"	Quartz test tube	Stirrer	11.7	19	30	"
4	"	Glass test tube	"	14.8	28	4	"
5	Not irradiated (in the dark)	"	Vibratory machine	5.2	48	Less than 1	"
6	"	"	"	5.2	120	5	"
7	"	"	"	5.2	600	32	"

toluene. Heating of the reaction mixture on a water bath resulted in elimination of mercuric halide and formation of two products: the C-acetyl(phenyl)acetic ester I and the acetate of the enol form of phenylacetic ester (II):



Formation of the substance (II) was shown by the fact that phenylacetic ester and acetic acid are formed by treatment of the mixture of (I) and (II) with a 2.5% aqueous solution of caustic potash in the cold:



$$C_6H_5-CH=C(OCOCH_3)(OC_2H_5) + KOH \rightarrow C_6H_5CH_2COOC_2H_5 + CH_3COOK.$$

Thus, in contrast with α-mercurated aldehydes and ketones, which react with acid chlorides with exclusive formation of vinyl esters [10, 11], for example:

$$ClHgCH_2CHO + CH_3COCl \rightarrow CH_2=CH-OCOCH_3 + HgCl_2,$$

the (bromomercuri)phenylacetic ester reacted with acetyl chloride with formation of both an O-derivative (with transfer of the reactive center) and a C-derivative (without transfer of the reactive center).

An attempt to prepare the simplest α-mercurated ester from ethyl bromoacetate was not successful. When the reaction mixture was exposed to ultraviolet radiation, only very small amounts of mercurous and mercuric bromides were formed.

On the other hand, ethyl iodoacetate reacted with mercury when irradiated, giving ethyl iodomercuriacetate, although in low yield:

$$I{-}CH_2COOC_2H_5 + Hg \xrightarrow{h\nu} I{-}Hg{-}CH_2{-}COOC_2H_5.$$

Even aromatic iodine derivatives reacted with mercury when exposed to ultraviolet radiation, giving the corresponding organomercury compounds *, for example,

$$C_6H_5I + Hg \xrightarrow{h\nu} C_6H_5HgI; \qquad \alpha\text{-}C_{10}H_7I + Hg \xrightarrow{h\nu} \alpha\text{-}C_{10}H_7HgI.$$

When mercury reacted with polybromo- and polychloro-methanes, no organomercury compounds were formed. Bromoform reacted slowly with mercury, even without irradiation, the reaction being appreciably accelerated in presence of benzoyl peroxide or by exposure to ultraviolet radiation. Formation then occurred of a mixture of mercurous and mercuric bromides, and also of small amounts of pentabromoethane as a result of secondary processes.

Boiling carbon tetrachloride did not react to an appreciable extent with mercury. The reaction went slowly in the presence of ultraviolet radiation at room temperature, and more rapidly at the boiling point of carbon tetrachloride in the presence of benzoyl peroxide, or when a mixture of carbon tetrachloride with mercury applied on barium sulfate was heated in a sealed tube at 120-130°:

$$2CCl_4 + 2Hg \longrightarrow CCl_3{-}CCl_3 + Hg_2Cl_2.$$

Chloroform, like carbon tetrachloride, reacted very slowly with mercury when irradiated without being heated; it formed calomel. Other cases that we have studied of the reactions of halogen compounds with mercury are given in Table 2.

Formation of organomercury compounds probably proceeds as a result of homolytic reaction, which may be represented as follows:

$$\left.\begin{array}{l} R{:}X \xrightarrow{h\nu} R\cdot + \cdot X \\ R{:}X + \cdot Hg\cdot \longrightarrow R\cdot + \cdot HgX \end{array}\right\} \text{or} \qquad \text{(I)}$$

$$R\cdot + \cdot Hg\cdot \longrightarrow R{-}Hg\cdot \qquad \text{(II)}$$

$$R{-}Hg\cdot + X{:}R \longrightarrow R{-}HgX + \cdot R \qquad \text{(III)}$$

According to the nature of the radical and of the halogen, various side reactions may occur in varying degree (dimerization of the radicals, their reaction with molecules of halogen derivative, etc.).

EXPERIMENTAL **

1. Reaction of Allyl Bromide with Mercury

a) A mechanically shaken mixture of allyl bromide (10 g) and mercury (34 g: a two-fold excess), contained in a quartz test tube, was exposed for 48 hours to ultraviolet radiation.*** From the reaction mixture, which had become thick, unchanged allyl bromide was distilled off, and the residue was extracted with acetone. After evaporation of the acetone, the dry residue was extracted with alcohol, yielding allylmercury bromide (2.4 g, 9%). The alcohol-insoluble residue had a low indefinite melting point and was evidently a polymer of allylmercury bromide. Allylmercury bromide dissolves readily in acetone, dioxane, and allyl bromide, poorly in ether, and is insoluble in petroleum ether Melting point (from aqueous alcohol) 116-118° (when heated rapidly). When the capillary is heated slowly, the substance is converted into an infusible polymer. Analysis for mercury gave somewhat high results, for, on being heated with hydrochloric acid, the substance was partially carbonized.

Found %: C 11.26; 11.08; H 1.70; 1.78
C_3H_5HgBr. Calculated %: C 11.18 H 1.55

The literature [12] gives m.p. 124-125°.

b) A mechanically shaken mixture of allyl bromide (11 g) and mercury (36 g; a two-fold excess) was irradiated in a glass test tube for 48 hours. The reaction mixture, treated as in the previous experiment, yielded 6.3 g (20%) of allylmercury bromide. No appreciable amounts of polymeric organomercury compounds were formed in this or the three following experiments

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* Almost simultaneously with us [9], Razuvaev and Shubenko [17] effected the synthesis of phenylmercury iodide from iodobenzene and mercury in the presence of radiation.

** The students M. A. Besprozvanny and S. S. Poddubnaya assisted in the performance of the experiments.

*** In all cases irradiation was carried out with the aid of a quartz mercury lamp PRK-4, the tube of which was placed at 20 cm from the reaction vessel.

c) A mixture of allyl bromide (11.7 g) and mercury (60 g: a three-fold excess) was irradiated for 19 hours while being stirred in a quartz test tube provided with a reflux condenser and a stirrer made from a bottle brush. When reaction was complete, the usual treatment yielded 9.3 g (30%) of allylmercury bromide

TABLE 2

Reaction of Organic Halogen Derivatives with Mercury

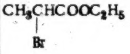
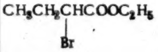
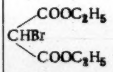
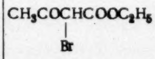
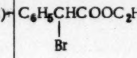
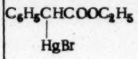
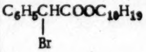
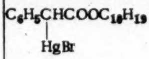
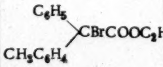
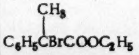
Original halogen derivative		Reaction conditions	Organomercury compound formed	Yield (%)	Other reaction products
Name	Formula				
Allyl bromide	$CH_2{=}CHCH_2Br$	Not irradiated, room temperature	$CH_2{=}CHCH_2HgBr$	32	None
Allyl chloride	$CH_2{=}CHCH_2Cl$	Irradiated, 40°	None	–	Hg_2Cl_2
Cinnamyl bromide	$C_6H_5CH{=}CHCH_2Br$	Not irradiated, room temperature	$C_6H_5CH{=}CHCH_2HgBr$	82	None
Cinnamyl chloride	$C_6H_5CH{=}CHCH_2Cl$	"	None	–	None
		Irradiated, 40°	None	–	Hg_2Cl_2, polymerization products of original substance.
Benzyl bromide	$C_6H_5CH_2Br$	a) Not irradiated, room temp.	None	–	None
		b) Not irradiated, 80°.	None	–	Hg_2Br_2, $HgBr_2$, HBr, resin
		c) Irradiated, room temp.	None	–	Hg_2Br_2, $HgBr_2$, HBr, resin
(2-Bromoethyl)benzene	$C_6H_5CHBrCH_3$	Irradiated, 40°	None	–	Hg_2Br_2, HBr, resin
Ethyl 2-bromopropionate	 $CH_3\underset{Br}{\underset{\mid}{C}}HCOOC_2H_5$	Irradiated, 40°	None	–	Hg_2Br_2
Ethyl 2-bromobutyrate	 $CH_3CH_2\underset{Br}{\underset{\mid}{C}}HCOOC_2H_5$	Irradiated, 40°	None	–	Hg_2Br_2
Diethyl bromomalonate	 $CHBr(COOC_2H_5)_2$	Irradiated, 40°	Organomercury polymer	–	None
Ethyl 2-bromoacetoacetate	 $CH_3CO\underset{Br}{\underset{\mid}{C}}HCOOC_2H_5$	Not irradiated, room temperature	Organomercury polymer	–	None
Ethyl bromo(phenyl)acetate	 $C_6H_5\underset{Br}{\underset{\mid}{C}}HCOOC_2H_5$	Not irradiated, room temperature	 $C_6H_5\underset{HgBr}{\underset{\mid}{C}}HCOOC_2H_5$	73	None
(l)-Menthyl bromo(phenyl)acetate	 $C_6H_5\underset{Br}{\underset{\mid}{C}}HCOOC_{10}H_{19}$	Not irradiated, room temperature	 $C_6H_5\underset{HgBr}{\underset{\mid}{C}}HCOOC_{10}H_{19}$	31	None
Ethyl bromo(phenyl)-p-tolylacetate	 $(C_6H_5)(CH_3C_6H_4)CBrCOOC_2H_5$	Not irradiated, room temperature	None	–	None
Ethyl 2-bromo-2-phenylpropionate	 $C_6H_5\overset{CH_3}{\overset{\mid}{C}}BrCOOC_2H_5$	Not irradiated, room temperature	None	–	None
Ethyl bromoacetate	$BrCH_2COOC_2H_5$	Irradiated, 40°	None	–	Hg_2Br_2, $HgBr_2$
Ethyl iodoacetate	$ICH_2COOC_2H_5$	Irradiated, 40°	$IHgCH_2COOC_2H_5$	–	Hg_2I_2, HgI_2
2-Bromopropionaldehyde	$CH_3CHBrCHO$	Irradiated, 40°	None	–	Hg_2Br_2, $HgBr_2$

TABLE 2 -- (continued)

Original halogen derivative		Reaction conditions	Organomercury compound formed	Yield (%)	Other reaction products
Name	Formula				
Bromo(phenyl)-acetaldehyde	$C_6H_5CHBrCHO$	Not irradiated, room temperature	Organomercury polymer	—	None
Bromomethyl phenyl ketone	$C_6H_5COCH_2Br$	Irradiated, 60°	None	—	None
Bromoform	$CHBr_3$	a) Not irradiated, 100°	None	—	Hg_2Br_2, $HgBr_2$, CBr_3-CHBr_2
		b) Irradiated, 40°	None	—	Ditto
Chloroform	$CHCl_3$	Irradiated, 40°	None	—	Hg_2Cl_2
Carbon tetrachloride	CCl_4	a) Boiling in presence of benzoyl peroxide	None	—	Ditto
		b) Heating in sealed tubes (120-130°)	None	—	Ditto
Iodobenzene	C_6H_5I	Irradiated, 40°	C_6H_5HgI	8	Hg_2I_2
1-Iodonaphthalene	α-$C_{10}H_7I$	Irradiated, 40°	α-$C_{10}H_7HgI$	6-8	Hg_2I_2

d) A mixture of allyl bromide (14.8 g) and mercury (47 g: a two-fold excess) was irradiated for 28 hours while being stirred in a glass test tube provided with a reflux condenser and a stirrer made from a bottle brush. The usual treatment yielded 1.5 g (4%) of allylmercury bromide.

e) A mixture of allyl bromide (5.2 g) and mercury (22 g: 150% excess) was shaken for 600 hours in a test tube wrapped in black paper. The usual treatment yielded 4.5 g (32%) of allylmercury bromide. When this experiment was carried out for 120 hours, allylmercury bromide was formed in 5% yield; and when it was carried out for 48 hours, the yield of organomercury compound was less than 1%.

2. Reaction of Cinnamyl Bromide with Mercury

Cinnamyl bromide (19.7 g = 0.1 mole) was mixed with an equal volume of 96% ethanol and with 100.3 g (0.5 g-atom) of mercury. After being shaken vigorously for 15 minutes the reaction mixture became slightly warm and thickened. Unchanged mercury was poured off, and ethanol was added to the mixture until a slurry was formed. The precipitate was filtered off, and the organomercury compound was extracted from it with benzene. The benzene solution was evaporated until crystallization began, and when crystallization was complete (2-3 hours) the cinnamylmercury bromide was filtered off under suction and washed with cold benzene; the yield was 32.7 g (82%). The substance was obtained in the form of creamy white scales, readily soluble in cold acetone, hot benzene, hot methanol, and hot ethanol, poorly soluble in cold benzene, cold methanol, and cold ethanol. Benzene was found to be the most satisfactory solvent for crystallization purposes: when crystallization was carried out from methanol or ethanol, the substance underwent appreciable decomposition with separation of mercury and formation of polymeric products. When heated quickly, the substance melted at 340-345°, but when heated slowly in the capillary it polymerized without melting. This substance is described for the first time.

Found %: C 27.33; 27.15; H 2.41; 2.49
C_9H_9HgBr. Calculated %: C 27.18; H 2.28

Found %: Hg 50.42; 50.34
C_9H_9HgBr. Calculated %: Hg 50.45

3. Reaction of Ethyl Bromo(phenyl)acetate with Mercury

A mixture of 150 g (0.617 mole) of ethyl bromo(phenyl)acetate and 480 g (2.38 g-atoms) was shaken for 30 minutes in a flask having a ground-in stopper. When the mixture had set solid, it was allowed to stand for 2-3 hours. The organomercury compound was extracted with boiling chloroform. The crystals obtained after evaporation of the chloroform were washed with a small amount of carbon tetrachloride to remove unchanged ethyl bromo(phenyl)acetate and then crystallized from ethanol. The yield was 200 g (73%); m.p. 125-126°. Ethyl (bromomercuri)phenylacetate is readily soluble in chloroform, hot acetone, and hot ethanol; not so soluble in benzene, cold ethanol, and carbon tetrachloride; insoluble in petroleum ether. It is readily decomposed by concentrated hydrochloric acid with formation of ethyl phenylacetate and mercuric chloride. The substance is described for the first time.

Found %: Hg 45.42; 45.72
$C_{10}H_{11}O_2HgBr$. Calculated %: Hg 45.21

4. Reaction of (l)-Menthyl Bromo(phenyl)acetate with Mercury

A mixture of 33.4 g (0.09 mole) of (l)-menthyl bromo(phenyl)acetate* and 135 g (0.68 g-atom) of mercury was shaken for 30 minutes. When the reaction mixture had become solid, it was set aside for 2-3 hours, and was then extracted with acetone. The acetone was evaporated off, and the residue was washed with cold alcohol. Mp. (from alcohol) 158-161°; yield 15.5 g (31%). The substance is described for the first time.

Found %: C 39.02; 39.14; H 4.59; 4.55
$C_{18}H_{25}O_2HgBr$. Calculated %: C 39.03; H 4.55

5. Symmetrization of Ethyl (Bromomercuri)phenylacetate

A stream of dry ammonia was passed for 10 minutes into a solution of ethyl (bromomercuri)phenylacetate (8 g) in dry chloroform. The precipitated bromoamidomercury (about 3.5 g) was filtered off, and chloroform was removed from the filtrate under suction. The oil remaining after removal of chloroform crystallized on standing (20-30 hours). The substance was washed with cold petroleum ether and cold methanol. M.p. after two recrystallizations from methanol 105.5-106.5°; yield 2 0 g (42%). The substance is described for the first time.

Found %: Hg 38.39; 38.44
$C_{20}H_{22}O_4Hg$. Calculated %: Hg 38.12

6. Reaction of Ethyl (Bromomercuri)phenylacetate with Acetyl Chloride

Doubly distilled acetyl chloride (31.4 g = 0.4 mole) was added to a suspension of 88.72 g (0.2 mole) of ethyl (bromomercuri)phenylacetate in dry toluene (100 ml). There was no reaction in the cold, and the mixture was heated on a water bath and boiled for two hours, care being taken to exclude moisture The inorganic precipitate (mercuric halide, 49.2 g) was filtered off, and excess of acetyl chloride, acetic acid, and a great part of the toluene were driven from the filtrate (which was light brown) at atmospheric pressure. The residue was distilled under 18 mm pressure, two fractions being collected:

Fraction I: B.p. 121-125°, 11.8 g
Fraction II: B.p. 140-160°, 10.4 g

Fraction I boiled mainly at 225-226° under normal pressure and was ethyl phenylacetate. Fraction II was a liquid that rapidly decolorized an alkaline solution of permanganate and a solution of bromine in carbon tetrachloride; its alcoholic solution became violet when ferric chloride was added. With phenylhydrazine in alcoholic solution the phenylhydrazone of ethyl 2-phenylacetoacetate (m.p. 104°) was formed, and the latter, on being heated, yielded 3-methyl-1,4-diphenyl-2-pyrazolin-5-one, melting, after being recrystallized twice from alcohol, at 195.5-196° (literature gives 196° [13]).

Found %: N 11.55; 11.34
$C_{16}H_{14}ON_2$. Calculated %: N 11.20

It was thus shown that Fraction II was the C-acetyl(phenyl)acetic ester. In order to find out whether there was any isomeric O-acetyl(phenyl)acetic ester in this fraction, 5 g of it was treated with excess of a 2.5% aqueous solution of KOH in the cold (the mixture was shaken for one hour and then set aside for one day). The oil (1.2 g) that formed on standing, which was found to be ethyl phenylacetate, was separated and hydrolyzed by heating with alkali, yielding phenylacetic acid (0.7 g), m.p. 76° after recrystallization from ligroin. It was concluded on the basis of the yield of phenylacetic ester that Fraction II contained at least 30% of the acetyl derivative of the enol form of phenylacetic ester.

7. Reaction of Ethyl Iodoacetate with Mercury in Presence of Ultraviolet Radiation.

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* A freshly prepared (liquid) mixture of diastereoisomers was employed.

A mixture of 5 g of ethyl iodoacetate, 15 ml of dry benzene, and 25 g of mercury was placed in a quartz test tube. The reaction mixture was irradiated for 16 hours with ultraviolet radiation, agitation being provided by a stirrer made from a bottle brush. The inorganic precipitate, consisting of unchanged mercury, mercurous iodide, and mercuric iodide, was filtered off and washed with benzene Benzene was removed from the filtrate under reduced pressure. The oil remaining after removal of benzene crystallized after standing for two weeks in a vacuum desiccator. The crystals were transferred to a porous plate and pressed out. They were recrystallized from methanol. Yield 0.2 g; m.p. 56-57°.

Ethyl iodomercuriacetate is a yellow crystalline substance, readily soluble in hot methanol and hot ethanol, soluble also in acetone and ethyl iodoacetate. Cold concentrated hydrochloric acid decomposes it with formation of mercuric iodide. The substance is described for the first time.

Found %: C 11.50; 11.33; H 1.78; 1.77

$IHgCH_2CO_2C_2H_5$. Calculated %: C 11.57; H 1.72

8. Reaction of Iodobenzene with Mercury

Iodobenzene (10.2 g = 0.05 mole) and mercury (50 g = 0.25 g-atom) were placed in a quartz test tube fitted with a stirrer made from a bottle brush. The mixture was irradiated for 40 hours while being stirred. The precipitate was then filtered off, washed with petroleum ether, and extracted with acetone. Evaporation of the acetone yielded a residue of 1.6 g (8%) of phenylmercury iodide, melting after crystallization from benzene at 266°. (Literature gives 266° [14]). The melting point of a mixture with authentic phenylmercury iodide was not depressed. In addition to phenylmercury iodide, some mercurous iodide was formed.

9. Reaction of 1-Iodonaphthalene with Mercury

A mixture of 12.7 g (0.05 mole) of 1-iodonaphthalene and 50 g (0.25 g-atom) of mercury was shaken for 50 hours in a quartz test tube. The reaction mixture, on being treated as in the previous experiment, yielded 1.4g (6%) of 1-naphthylmercury iodide, melting after crystallization from a mixture of benzene and alcohol at 184.5° (literature gives 185° [14]). In addition to 1-naphthylmercury iodide, some mercurous iodide was formed

10. Reaction of Polyhalomethanes with Mercury

a) Reaction of bromoform with mercury in presence of benzoyl peroxide. In a flask fitted with stirrer and dropping funnel, a stirred mixture of 126.5 g (0.5 mole) of bromoform, 20 g (0.1 g-atom) of mercury carried on barium sulfate, and 0.5 g of benzoyl peroxide was heated in a boiling water bath for 8-10 hours, and then, on three occasions separated by intervals of 2-3 hours, a solution of benzoyl peroxide (0.5 g) in bromoform (10 ml) was added. Reaction was complete in 16-20 hours (the precipitate became white). The precipitate was filtered off and extracted with acetone: mercuric bromide (7.0 g) passed into the acetone, and the residue was a mixture of mercurous bromide and barium sulfate. Bromoform was driven from the filtrate (60 mm, 67°), and the residue was found to be impure benzoic acid.

b) Reaction of bromoform with mercury in presence of radiation . A stirred mixture of 126.5 g (0.5 mole) of bromoform and 20 g (0.1 g-atom) of mercury carried on barium sulfate, containing in a quartz flask, was exposed to ultraviolet radiation. Reaction was complete in 28 hours. The reaction mixture was diluted with ether, and the precipitate, consisting of mercuric bromide, mercurous bromide, and barium sulfate, was filtered off. Ether was removed from the filtrate at ordinary pressure, and bromoform was removed at 60 mm. The residue, pentabromoethane, came over at 120°/12 mm; yield 0.5 g; m.p. 52-53° (literature gives 54° [15]).

c) Reaction of bromoform with mercury at 100°. A mixture of bromoform (126.5 g) and mercury (20 g) carried on barium sulfate was heated on a boiling water bath until the precipitate became white (about 60 hours). The reaction mixture was treated as in the previous experiment: mercuric and mercurous bromides were isolated; also 0.3 g of pentabromoethane.

d) Reaction of carbon tetrachloride with mercury in presence of benzoyl peroxide. A mixture of carbon tetrachloride (100 g), mercury (20 g) carried on barium sulfate, and benzoyl peroxide (1 g) was placed in a flask provided with stirrer and a condenser protected by a calcium chloride tube The reaction mixture was heated at the boil and was stirred continuously, and two 0.5-g portions of benzoyl peroxide were added at intervals of 15 hours. The precipitate became pure white after 50 hours, and it was found to consist of calomel and barium sulfate. The filtrate was evaporated down, and the residue, consisting of hexachloroethane, was distilled (yield 1.5 g). After a second distillation it melted at 185.5-186.5° (literature gives 186.85-187.40° [16]).

e) Reaction of carbon tetrachloride with mercury at 120-130°. A mixture of 77 g (0.5 mole) of carbon tetrachloride and 100 g (0.5 g-atom) of mercury carried on barium sulfate was heated in a sealed tube for 40 hours at 120-130°. When the tube was opened, a small amount of hydrogen chloride was evolved The contents of the tube were diluted with ether, and the precipitate, which consisted of calomel and barium sulfate, was filtered off. The ether solution was evaporated down, and the residue was distilled, yielding pure hexachloroethane (3.5 g, 6 %).

SUMMARY

1. The reactions of several aliphatic and aromatic halogen derivatives with mercury have been investigated.

2. It has been shown that reaction of halogen derivatives with mercury is activated by ultraviolet radiation and by benzoyl peroxide, a fact that is an argument in favor of a homolytic mechanism for these reactions.

3. It has been found that aromatic iodine derivatives, and also aliphatic and aliphatic-aromatic bromine derivatives, can react with mercury with formation of organomercury compounds.

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PRINCIPLES OF THE NOMENCLATURE AND CLASSIFICATION OF MACROMOLECULAR ORGANOSILICON COMPOUNDS

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During the last two decades the chemistry of macromolecular organosilicon compounds has established itself as a feature of the utmost importance in the present and future development of organosilicon chemistry. For its further successful development it is essential to systematize the material that has already accumulated and to work out a scheme of nomenclature and classification of macromolecular organosilicon compounds. The development of a nomenclature and classification for this important section of organosilicon chemistry will facilitate its study and further progress. The names of macromolecular organosilicon compounds are at present formed without any definite system, and they are very often arbitrary and do not reflect the chemical structure of the macromolecular organosilicon compound; it is therefore impossible to get any idea from these names of the properties and possible chemical reactions of the substances. No schemes of nomenclature and classification of macromolecular organosilicon compounds have yet been proposed in the literature.

In one of our papers we have stated the basic principles of our proposed nomenclature and classification of low-molecular-weight organosilicon compounds [1]. It is proposed that our rational nomenclature for macromolecular organosilicon compounds should be based on the structure of the main chain of the macromolecule. The names of macromolecular organosilicon compounds are made up of: numbers and names of end groups; names of groups, radicals, or atoms bound to silicon or other atoms forming links in the chain molecule, with indications of their numbers; names of groups, radicals, or atoms from which the chain of the macromolecule is built up. The number of links in the chain is denoted by the prefix "poly". For end groups an indication is given for their position at the first and terminal atom, namely (1−n). The names of copolymers are built up in a similar way. The silicon atom is called "silane".

Our classification of macromolecular organosilicon compounds is based on the structure of the main chain of the molecule As a starting point for the classification we take the sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$, and all other macromolecular organosilicon compounds are regarded as derivatives of this substance, i.e., as substances formed from it by replacement of hydrogen atoms by organic radicals or groups and, for certain classes of compounds, by simultaneous replacement of Si−Si links by bivalent radicals, oxygen, or amino group (−NH−), etc.

When in a polymeric silahydrocarbon hydrogen is replaced by radicals or groups, for example:

	Radicals	**Groups**
Methyl CH_3-	Chloromethyl $ClCH_2-$	Methoxy CH_3O-
Ethyl C_2H_5-	Chloroethyl $ClCH_2CH_2-$	Ethoxy C_2H_5O-
Propyl C_3H_7-	Chlorophenyl ClC_6H_4-	Phenoxy C_6H_5O-
Butyl C_4H_9-	Vinyl $CH_2=CH-$	Anilino C_6H_5NH- etc.
Phenyl C_6H_5-	Ethynyl $CH\equiv C-$ etc.	

with simultaneous replacement of Si−Si bonds by bivalent radicals (−R−) or bivalent groups (−NH−; −OM"−, where M is a metal), or by oxygen atoms, various classes of macromolecular organosilicon compounds are accordingly formed.

The following division into classes is the one that accords most satisfactorily with the present position of the study of macromolecular organosilicon compounds.

1. Silanochain polymers or alkyl(aryl)polysilanes. Silanochain polymers are substances in which the molecular chain is composed entirely of silicon atoms. Substances of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2-]_xSiH_3$ by organic radicals or groups. Their names are built up from the numbers and names of end groups, the names of radicals or groups (the number that occur in the unit of the chain molecule is indicated), the names of atoms from which the main chain of the polymer molecule is built, and the prefix "poly", for example:

$(CH_3)_3Si-[Si(CH_3)_2]_x\ Si(CH_3)_3$
(1−n) Hexamethylpolydimethylsilane
$(CH_3)_3Si\ [-C_6H_5\ SiCH_3-]_x\ Si(CH_3)_3$
(1−n) Hexamethylpolyphenylmethylsilane
$(SiC_6H_5CH_3)_x$
Polyphenylmethylsilane

Compounds of this class are obtained by the action of alkali metals on alkyl(aryl)halosilanes, and also by other methods. The silicon chain is destroyed by hydrolysis, especially in an alkaline medium. On pyrolysis, silanochain polymers decompose with formation of low-molecular-weight products, readily oxidized by air.

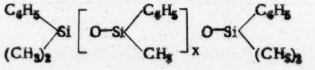
2. Carbosilanochain polymers or organopolyalkyl(aryl)silanes. Carbosilanochain polymers are substances in which the molecular chain is composed of carbon and silicon atoms. Compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2-]_x\ SiH_3$ by radicals or groups, with simultaneous replacement of Si−Si links by bivalent alkyl or aryl radicals. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals or groups of the unit of the chain molecule, and names of radicals and atoms from which the chain of the macromolecule is built, for example:

$(CH_3)_3Si-[CH_2-Si(CH_3)_2-]_x\ CH_2-Si(CH_3)_3$
(1−n)Hexamethylpolydimethylmethylenesilane
$(CH_3)_3Si\ [-CH_2-CH_2-Si(C_2H_5)_2-]_x\ C_2H_4-Si(CH_3)_3$
(1−n)Hexamethylpolydiethylethylenesilane
$(CH_3)Si-[C_6H_4-Si(CH_3)_2]_x-C_6H_4-Si(CH_3)_3$
(1−n)Hexamethylpolydimethylphenylenesilane

Compounds of this class are prepared by the action of alkali metals, etc., on alkyl(aryl)halosilanes and dihalo derivatives. The silicon-carbon polymer chain is not broken down hydrolytically by water. On pyrolysis, carbosilanochain polymers very often form low-molecular-weight polymeric compounds having chains of similar structure.

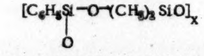
3. Oxygenosilanochain polymers or organopolyalkyl(aryl)siloxanes. Organopolyalkyl(aryl)siloxanes are substances in which the molecular chain is composed of oxygen and silicon atoms. Compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si−Si links by oxygen. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals and groups attached to silicon in the unit of the chain, and names of radicals and atoms from which the chain of the macromolecule is built:

$(CH_3)_3Si\ [-OSi(CH_3)_2-]_x-O-Si(CH_3)_3$
(1−n) Hexamethylpolydimethylsiloxane



(1−n) Diphenyltetramethylpolyphenylmethylsiloxane

$(CH_3SiO_{1.5})_x$
Polymethylsiloxane
$[(CH_3)_2SiO]_x$
Polydimethylsiloxane



$[C_6H_5\underset{\underset{O}{|}}{Si}-O-(CH_3)_2\ SiO]_x$

Polyphenyldimethyldisiloxane
$(CH_3O)_3Si-[OSi(CH_3)_2]_x\ OSi(OCH_3)_3$
(1−n) Hexamethoxypolydimethylsiloxane
$(C_2H_5O)_3Si-[OSi(OC_2H_5)_2-]_x\ OSi(OC_2H_5)_3$
(1−n) Hexaethoxypolydiethoxysiloxane
$[Si(OC_2H_5)_2O]_x$
Polydiethoxysiloxane

Compounds of this class are obtained by hydrolysis with water of organohalosilanes, organo-substituted esters of silicic acid, and other compounds containing groups attached to silicon that may be split off by hydrolysis; they may be prepared also by other methods. The oxygenosilane chain of the polymer is not broken down by hydrolysis. Organopolyalkyl(aryl)siloxanes are heat-stable compounds, but at very high temperatures linear polymers depolymerize, often forming low-molecular-weight compounds $(R_2SiO)_x$, where x = 3, 4, 5, 6, etc. On pyrolysis in presence of air, they may be converted into a three-dimensional polymer owing to removal of organic groups and formation of Si—O linkages.

4. Carbonsiloxanochain polymers or organopolyalkyl(aryl)carbosiloxanes. Carbonsiloxanochain polymers are substances in which the molecular chain is composed of carbon, silicon, and oxygen. Compounds of this class are formed by replacement of hydrogens in the sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by organic radicals or groups, with simultaneous replacement of Si—Si links by organic bivalent radicals and oxygen. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals and groups attached to silicon in the unit of the chain, and names of radicals and atoms from which the chain of the macromolecule is built, for example:

$$(CH_3)_3Si[-C_6H_4-Si(CH_3)_2OSi(CH_3)_2]_x-C_6H_4-Si(CH_3)_3$$

(1—n) Hexamethylpolytetradimethylphenylenedisiloxane

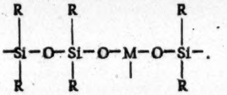
$$(CH_3O)_3Si[CH_2-Si(CH_3)_2OSi(CH_3)_2]_x-CH_2-Si(OCH_3)_3$$

(1—n) Hexamethoxypolytetramethylmethylenedisiloxane

Compounds of this class are obtained by the action of alkali metals on organohalosilanes and organohalodisiloxanes; they may be prepared also by other methods. The chains of these molecules are not broken down by hydrolysis with water; they are stable to heat, but at high temperatures they undergo pyrolysis with breakdown of the main chain of the molecule.

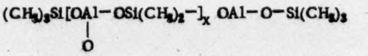
5. Metallooxygensilanochain polymers or organopolyalkyl(aryl)metallosiloxanes. Metallooxygensilanochain polymers are substances in which the molecular chain is composed of metal atoms, oxygen, and silicon. The metal may be a bi- or multi-valent metal, such as magnesium, aluminum, chromium, lead, tin, etc.

The chain of the molecule can be represented as follows:



$$-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{Si}}-O-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{Si}}-O-\underset{|}{M}-O-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{Si}}-.$$

Compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by oxygen $\underline{O}$ or by the —OM—group, where $\underline{M}$ is a bi- or multi-valent metal. The names of compounds of this class are built up from the names and numbers of end groups, the prefix "poly", the numbers and names of radicals or groups attached to silicon or metal atoms in the unit of the polymer chain, and names of atoms from which the chain of the macromolecule is built, for example:



$$(CH_3)_3Si[\underset{\underset{O}{|}}{OAl}-OSi(CH_3)_2-]_x\,OAl-O-Si(CH_3)_3$$

(1—n) Hexamethylpolydimethylaluminosiloxane

$$(C_2H_5O)_3Si[OMgOSi(OC_2H_5)_2]_x-OMgOSi(OC_2H_5)_3$$

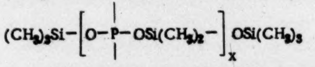
(1—n) Hexaethoxypolydiethoxymagnesiumsiloxane

6. Metalloidoxygensilanochain polymers or organopolyalkyl(aryl)metalloidsiloxanes. Metalloidoxygensilanochain polymers are substances in which the molecular chain is composed of atoms of nitrogen, oxygen, or other metalloid (phosphorus, sulfur, etc.) and silicon atoms. Polymeric compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by metalloid atoms, e.g. S, or a metalloid group, e.g. —NH—, —OPO—, etc.

The names of macromolecular organosilicon compounds of this class are built up from the names and numbers of end groups, the prefix "poly", the numbers and names of radicals and groups attached to silicon and metalloid atoms in the unit of the chain polymers, and names of atoms and metalloid groups from which the chain of the macromolecule is built, for example:

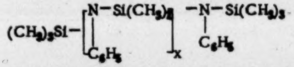
$(CH_3)_3Si[NH-Si(CH_3)_2]_xNH-Si(CH_3)_2$

(1–n) Hexamethylpolydimethylaminosilane



$(CH_3)_3Si-\left[O-\overset{|}{\underset{|}{P}}-OSi(CH_3)_2-\right]_xOSi(CH_3)_3$

(1–n) Hexamethylpolydimethylphosphorsiloxane



$(CH_3)_3Si-\left[\underset{C_6H_5}{N}-Si(CH_3)_2\right]_x-\underset{C_6H_5}{N}-Si(CH_3)_3$

(1–n) Hexamethylpolydimethylphenylaminosilane

Compounds of this class have received little study: only a few are known. High polymers containing nitrogen are obtained by the action of ammonia or amines on alkylarylhalosilanes. Compounds containing phosphorus in the main chain are obtained by the action of phosphoric anhydride or phosphoric esters on organosilicon compounds containing hydroxyl groups attached to silicon, etc. The chains of these molecules are broken down by hydrolysis with water. On pyrolysis, chain breakdown occurs.

The proposed scheme for the classification of macromolecular organosilicon compounds is not complete, being concerned with principles only: only linear and cyclic polymers have been referred to it, and ramified chains have not been considered, though there can be no doubt that they may be included in this classification.

Also, macromolecular organosilicon compounds containing not only groups or organic radicals, but simultaneously both groups and radicals, may equally readily be incorporated in the proposed scheme of classification. The introduction of any organic group into an organic radical attached to a silicon atom in the unit of the molecular chain does not change the class of the given substance, because the classification is based on the structure of the molecular chain.

All the properties of macromolecular organosilicon compounds are related, to a greater extent than for organic high polymers, to the structure of the main chain of the macromolecule, and classification of the polymers according to the structure of the molecular chain therefore permits their properties to be predicted.

SUMMARY

1. A nomenclature and classification has been proposed for macromolecular organosilicon compounds.

2. The proposed classification of macromolecular organosilicon compounds is based on the structure of the main chain of the molecule

3. The substance taken as the starting point for the classification is the polymeric sila hydrocarbon $H_3Si[SiH_2]_xSiH_3$, and all other macromolecular organosilicon compounds are treated as derivatives of this substance.

LITERATURE CITED

[1] A. V. Topchiev and K. A. Andrianov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 3, 490 (1953).*

Received September 11, 1952.

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* See Consultants Bureau Translation, page 439.

CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 2. HYDROGENATION OF ISOPRENE IN PRESENCE OF PLATINUM, PALLADIUM, AND NICKEL

B. A. Kazansky, I. V. Gostunskaya, and A. M. Granat

It has been shown by Kazansky and Popova [1] that when biisocrotyl (2,5-dimethyl-2,4-hexadiene) is hydrogenated in presence of platinum, palladium, or Raney nickel, addition of hydrogen occurs simultaneously in all possible ways, so that the hydrogenation of biisocrotyl must be classified, according to Lebedev's system, as 1,3-diene hydrogenation of the second type. Addition of hydrogen to biisocrotyl occurs predominantly in the 1,2-positions, although the extent to which it occurs in these positions depends on the nature of the catalyst. In addition to alkenes, a certain amount of the full-hydrogenation product, 2,5-dimethylhexane, is always formed at the same time; it is formed to the greatest extent in presence of platinum, which is the least selective of the catalysts in the hydrogenation, and to the least extent in presence of Raney nickel, when hydrogenation proceeds in the most selective fashion, the main reaction product (about 90%) being 2,5-dimethyl-2-hexene. The reaction-rate curves for the hydrogenation of biisocrotyl give little indication of the actual course of the reaction.

The effect of the nature of the catalyst on the manner in which hydrogen added to biisocrotyl, as observed in the work referred to, prompted us to carry out a comparative investigation of the hydrogenation of isoprene in presence of the same catalysts, in spite of the fact that this reaction in presence of platinum black had already been described (1928) by Lebedev and Yakubchik [2], who found that isoprene belongs to Lebedev's second type of dienes

Lebedev and Yakubchik did not isolate any individual hydrocarbons from the products of the 50% hydrogenation of isoprene, but, having first removed unchanged isoprene with the help of SO_2, they were able to form an idea of the nature of these hydrocarbons by analyzing the kinetic curves obtained for addition of hydrogen to these products to saturation and by determining the amount of hydrogen required (from the difference between the calculated volume of hydrogen and that actually found it was possible to estimate the content of isopentane in the products of the first stage of hydrogenation). By addition of 50% (one molecule) of hydrogen, isoprene may yield a mixture of 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene, and these may be further hydrogenated at different rates [3] giving rise to separate sections on the kinetic curves for the reaction. It was therefore possible, by adding definite amounts of 3-methyl-1-butene or 2-methyl-2-butene to the hydrogenation product freed from isoprene and then hydrogenating the mixture, to determine (by a comparison of the results found in this way with those obtained from the analysis of kinetic curves obtained without these additions) the contents of these hydrocarbons in the products under investigation.

On the basis of all the results obtained by this means, Lebedev and Yakubchik concluded that the composition of the product formed by the addition of one molecule of hydrogen to isoprene in presence of platinum black was:

Isoprene	30 mol.-%
Isopentane	30 "
3-Methyl-1-butene	12 "
2-Methyl-1-butene	13 "
2-Methyl-2-butene	15 "
	100 "

Apart from this work of Lebedev, there has been a study of the catalytic hydrogenation of isoprene by Dupont [4], who used Raney nickel as catalyst. The mixture of hydrogenation products that he obtained was investigated by the Raman spectra method, and it was found to contain equimolecular amounts of 3-methyl-1-butene and 2-methyl-2-butene. The absence in Dupont's hydrogenation products of 2-methyl-1-butene is puzzling and gives rise to some doubts concerning the accuracy of the analysis.

In the present investigation our object was the determination of the composition of the products of the addition of one molecule of hydrogen to isoprene in presence of platinum, palladium, and Raney nickel by separating the components of the mixture by distillation through a column having an efficiency of about 70 theoretical plates. The main difficulty that we have met has arisen from the volatility of the hydrocarbons (b.p. 20-39°), which resulted in losses during the treatment of the mixture (mainly during washing, separation, transference operations, etc.), in spite of the cooling employed. Since the losses during distillation through the columns were comparatively low, we consider that they may be assigned in more or less equal measure to all of the components of the mixture

As a result of rate measurements on the hydrogenation of isoprene in presence of the three catalysts, hydrogenation curves were obtained which differed from one another in character. The curves for hydrogenation in presence of platinum black had breaks corresponding to the addition of 70% hydrogen and the consumption of the whole of the isoprene; Lebedev called this point "the critical point for the hydrogenation of a conjugated system". The curves for hydrogenation of isoprene in presence of palladium black and Raney nickel showed one break, which in the case of palladium occurred somewhat beyond the point corresponding to the addition of one molecule of hydrogen (50%), and in the case of Raney nickel corresponded exactly to the addition of one molecule of hydrogen. It might have been supposed from the curves, following Lebedev's classification, that hydrogenation in presence of these two last catalysts proceeds in a fairly selective fashion, but a detailed investigation of the reaction products has shown that here, as in the case of platinum, the addition of hydrogen goes in all possible ways. The part played by the nature of the catalyst is to be seen first in the fact that during the addition of the first molecule of hydrogen the fully-saturated hydrocarbon is formed in smaller amount when palladium black or Raney nickel is used than when platinum black is used (2-3% instead of 25-30%), and second, in the fact that with different catalysts the three pentenes are formed in different proportions. Thus, in the case of platinum black the main reactions were 3,4-addition of hydrogen to form 2-methyl-1-butene and addition of two molecules of hydrogen to give isopentane; in the case of palladium black the main reaction was 1,4-addition of hydrogen with formation of 2-methyl-2-butene; and in the case of Raney nickel the main reaction was again 1,4-addition of hydrogen, but some 3,4-addition, with formation of 2-methyl-1-butene, occurred also.

In comparison with biisocrotyl, isoprene, which may be regarded as butadiene with one substituent on the second carbon atom, takes up more hydrogen at the first and fourth carbon atoms during hydrogenation; the difference is particularly notable when palladium and nickel catalysts are used. Similar peculiarities with respect to the direction of reaction, though in a more clearly expressed form, are observed for the addition of nascent hydrogen to these two hydrocarbons: under the action of hexamminecalcium biisocrotyl again unites with hydrogen mainly in the 1,2-positions [5] (the same is to be observed for reaction with the system sodium-liquid ammonia [6]); under these conditions isoprene unites with hydrogen mainly in the 1,4-positions [5].

EXPERIMENTAL

1. Characteristics of the isoprene used. The isoprene was distilled through a precision-rectification column of 70-plate efficiency, and it had the following properties: b.p. 33.5° at 750 mm; n_D^{20} 1.4224; d_4^{20} 0.6798; found MR 24.45; calculated for $C_5H_8 2F$ 24.33; molecular refraction increment 1.12. The literature [2] gives: b.p. 34.5° at 765 mm; n_D^{20} 1.42207; d_4^{20} 0.6803; found MR 24.40; calculated for $C_5H_8 2F$ 24.33.

2. Procedure for hydrogenation and in investigation of reaction products. The isoprene was hydrogenated at room temperature and atmospheric pressure in a long-necked flask shaken about 300 times (double shakes) per minute. The amount of hydrogen absorbed was measured in a 100-ml gas buret having 0.2-ml graduations. The readings required for constructing the hydrogenation curve were taken every 30 seconds. Completion of the addition of the first molecule of hydrogen is indicated on the hydrogenation curves by the symbol X.

Platinum and palladium blacks were prepared by Willstätter's method [7], and Raney nickel was prepared by Adkins' method [8]. The solvent was 96% alcohol. In experiments having as their object the study of the products resulting from the addition of one molecule of hydrogen to isoprene, the reaction was allowed to proceed until the calculated amount of hydrogen for the given weight of isoprene had been absorbed, and the catalyst was then filtered off and the alcoholic solution of the hydrogenation products was distilled through a column to separate the azeotropic mixtures of alcohol with hydrocarbons formed during the hydrogenation. The alcohol was washed out with cooled calcium chloride solution; isoprene was then removed from the mixtures of hydrocarbons formed in presence of platinum and palladium by treatment in accordance with the Diels-Alder reaction with maleic anhydride.

in a benzene medium, since the presence of isoprene would render the further separation of the mixture difficult; and the hydrocarbons were finally fractionated through a column of 70 theoretical plates. The hydrocarbons obtained were identified with the aid of determinations of the boiling points, refractive indices, densities, and bromine numbers of the fractions. Bromine numbers were determined by Kaufmann's method, as modified by Galpern and Vinogradova [10]. The amounts of various hydrocarbons obtained in the hydrogenation process were calculated by using the data supplied by the distillation curves and by making use of the properties of functions.

3. Hydrogenation of isoprene in presence of platinum black. The conditions under which the hydrogenation of isoprene was carried out in two experiments are given in Table 1.

TABLE 1

Expt. No.	Amt. of isoprene (mole)	Amt. of Pt (mole)	Amt. of alcohol (ml)	Temp. of expt. (°C)	Pressure (mm Hg)	Amt. of hydrogen (ml)	
						Absorbed	Calculated
1	0.0127	0.0011	25	19	748	670	618
2	0.0105	0.0012	25	22	754	536	512

The hydrogenation curve (Fig. 1) shows that the course of the process is complex. The addition of one molecule of hydrogen is not indicated in any way by the course of the curve; change in rate of hydrogenation begins after the addition of about 70% of hydrogen. As in the hydrogenation curve obtained by Lebedev, four sections can be distinguished in the curves obtained in the present work.

TABLE 2

Fraction No.	B.p. (°C/ 760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR		Bromine No.*	Amount	
					Found	Calc'd		of alkenes (%)	of isopentane (g)
I	19.9-27.7	3.2	1.3635**	0.6301**	–	–	99.0	43.2	1.8
II	27.8	2.5	1.3553**	0.6176**	25.44	25.29	18.5	8.1	2.3
III	27.9-31.1	3.6	1.3618	0.6284	–	(C_5H_{12})	67.1	29.4	2.5
IV	31.2	4.3	1.3780	0.6500	24.65	24.82 (C_5H_{10})	–	–	–
V	31.3-38.4	2.1	1.3844	0.6583	–	–	–	–	–
VI	38.4-39.9	2.4	1.3887	0.6606	–	–	–	–	–
Residue	–	5.0	1.5000	–	–	–	–	–	–

* In the bromine number column results are given only for the fractions containing saturated hydrocarbon; the bromine numbers of the remaining fractions are close to the theoretical values.

** At 15°.

In order to make a more detailed study of the hydrogenation of isoprene in presence of platinum black, a 50 % hydrogenation was carried out on 44.8 g of isoprene. After distillation, removal of alcohol by washing, and removal of isoprene by means of maleic anhydride, the mixture of hydrogenation products with an addition of benzene from the previous treatment was distilled through a column of 70 theoretical plates. Six fractions were obtained: their characteristics are given in Table 2, and the distillation curve is given in Fig. 2.

The physical properties of the hydrocarbons that may be formed by addition of hydrogen to isoprene are given in Table 3 [11].

By taking into account the properties of the fractions obtained and the properties of the hydrocarbons cited in Table 3, we may calculate the compositions of the mixtures of hydrogenation products.

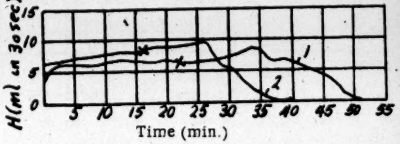

Fig. 1. Hydrogenation curves for isoprene in presence of platinum black: 1) Expt. 1; 2) expt. 2

Fraction I	contains 1.4 g 3-methyl-1-butene and 1.8 g isopentane
Fraction II	contains 0.2 g 3-methyl-1-butene and 2.3 g isopentane
Fraction III	contains 1.1 g 2-methyl-1-butene and 2.5 g isopentane
Fraction IV	contains 4.3 g 2-methyl-1-butene
Fraction V	contains 0.8 g 2-methyl-1-butene and 1.3 g 2-methyl-2-butene
Fraction VI	contains 2.4 g 2-methyl-2-butene

The residue in the flask is benzene.

Adding together the contents of each individual hydrocarbon in the various fractions and taking into account

TABLE 3

Hydrocarbon	B.p. (°C at 760 mm)	d_4^{20}	n_D^{20}
3-methyl-1-butene	20.1	0.6340 (15°)	1.3677 (15°)
2-methyl-1-butene	31.0	0.6504	1.3785
2-methyl-2-butene	38.6	0.6596	1.3876
Isopentane	27.9	0.6196	1.3579 (15°)

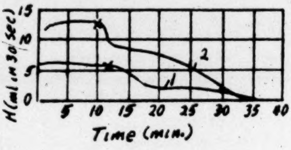

Fig. 3. Hydrogenation curves for isoprene in presence of palladium black: 1) Expt. 1; 2) Expt. 2.

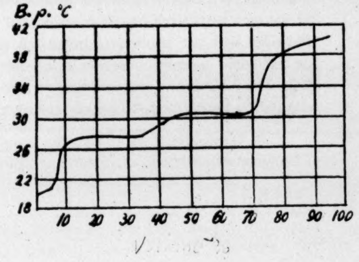

Fig. 2. Distillation curve for the product of the addition of one molecule of hydrogen to isoprene in presence of platinum.

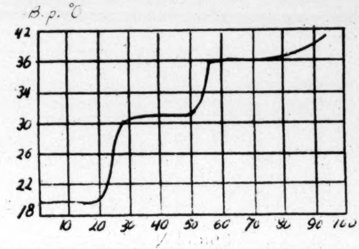

Fig. 4. Distillation curve for the product of the addition of one molecule of hydrogen in presence of palladium.

Lebedev's rule, namely that the molar quantities of diene and saturated hydrocarbons at the point at which one molecule of hydrogen has added to the diene are equal, we obtain the following composition for the mixture of hydrogenation products:

3-Methyl-1-butene	1.6 g	7.0 mol.%
2-Methyl-1-butene	6.2 g	26.0 "
2-Methyl-2-butene	3.7 g	15.0 "
Isoprene	6.2 g	26.0 "
Isopentane	6.6 g	26.0 "

It will be seen from this that 50% hydrogenation of isoprene in presence of platinum black proceeds in all theoretically possible directions, but the major products are isopentane and 2-methyl-1-butene, the product of the addition of one molecule of hydrogen in the 3,4-position of the conjugated system.

TABLE 4

Expt. No.	Amt. of isoprene (mole)	Amt. of Pd (mole)	Amt. of alcohol (ml)	Temp. (°C)	Pressure (mm Hg)	Amt. of hydrogen (ml)	
						Absorbed	Calculated
1	0.0060	0.0008	25	21.0	754	272	292
2	0.0103	0.0020	25	23.5	752	512	506

4. Hydrogenation of isoprene in presence of palladium black. The conditions under which the two experiments were carried out are given in Table 4.

The hydrogenation curves for isoprene in presence of palladium black (Fig. 3) show a break slightly beyond the point for the addition of one molecule of hydrogen. After the break the rate of hydrogenation falls sharply and then gradually. In order to make a more detailed study of the products of the addition of one molecule of hydrogen to isprene in presence of palladium, 44.3 g of isoprene was hydrogenated. The hydrogenation product was separated from alcoholic solution and freed from isoprene in the manner already described. Fractionation through a column of 70 theoretical plates gave the curve shown in Fig. 4. The results of the fractionation and the properties of the fractions obtained are given in Table 5.

On the basis of the properties of the fractions obtained, their bromine numbers, and the properties of the individual hydrocarbons that can be formed by hydrogenation of isoprene, a calculation was made of the composition of the mixture of hydrogenation products in the same way as that done for the platinum experiment. The results obtained were:

3-Methyl-1-butene	25 mol. %
2-Methyl-1-butene	30 "
2-Methyl-2-butene	41 "
Isopentane	2 "
Isoprene	2 "

Hydrogenation of isoprene in presence of palladium black proceeds therefore in all possible directions, but the main direction of the reaction is the addition of one molecule of hydrogen in the 1,4-position of the conjugated system with formation of 2-methyl-2-butene.

TABLE 5

Fraction No.	B.p. (°C/760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR found	MR calculated for C_5H_{10}	Bromine No.	Amount of alkenes (%)	Amount of isopentane (g)
I	20.1-20.2	2.9	1.3685 (15°)	0.6320 (15°)	24.92	24.82	—	—	—
II	20.3-28.6	1.3	1.3675 (15°)	0.6379 (15°)	—	—	198.3	84.1	0.2
III	28.7-30.9	1.0	1.3739	0.6489	—	—	—	—	0.2*
IV	31.0-31.1	2.9	1.3785	0.6506	24.82	—	—	—	—
V	31.2-38.3	2.3	1.3834	0.6566	—	—	—	—	—
VI	38.4-38.5	3.5	1.3879	0.6615	24.92	—	—	—	—
VII	38.6-40.0	1.8	1.3887	0.6618	—	—	—	—	—
	Residue	3.4	1.5022		—	—	—	—	—

TABLE 6

Expt. No.	Amt. of isoprene (mole)	Amt. of Ni(mole)	Amt. of alcohol (ml)	Temp. of expt. (°C)	Pressure (mm Hg)	Amt. of hydrogen (ml) absorbed	Amt. of hydrogen (ml) calculated
1	0.0066	0.0028	30	20.5	759	218**	318
2	0.0067	0.0015	30	20.8	748	190**	328

5. Hydrogenation of isoprene in presence of Raney nickel. The conditions under which the two experiments were carried out are given in Table 6.

The hydrogenation curves for isoprene in presence of a nickel catalyst are similar in character to those obtained in the presence of palladium black, but the break occurs exactly at the point corresponding to addition of one molecule of hydrogen to isoprene (Fig. 5).

TABLE 7

Fraction No.	B.p. (°C/760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR found	MR calculated for C_5H_{10}	Bromine No.	Amount of alkenes (%)	Amount of isopentane (g)
I	20.0-20.1	4.4	1.3672 (15°)	0.6316 (15°)	25.05	24.82	—	—	—
II	20.2-27.3	0.9	1.3636 (15°)	0.6305 (15°)	—	—	218.5	95.5	0.04
III	27.4-31.0	3.4	1.3712	0.6397	—	—	183.5	80.2	0.68
IV	31.1	9.1	1.3783	0.6502	24.84	—	—	—	—
V	31.2-38.3	4.0	1.3936***	0.6595	—	—	—	—	—
VI	38.4	10.8	1.3882	0.6606	25.00	—	—	—	—
VII	38.4-46.2	1.3	1.3883	0.6605	—	—	—	—	—

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* The content of saturated hydrocarbon in Fraction III was calculated from the density and refractive index, since it was not found possible to determine the bromine number of the fraction.

** In view of the fact that hydrogenation proceeded at a very low, but constant rate in its final stage, the reaction was not completed.

*** The high refractive index of Fraction V is to be explained by the presence of some isoprene as impurity.

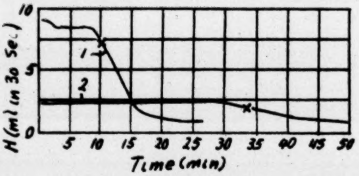

Fig. 5. Hydrogenation curves for isoprene in presence of Raney nickel: 1) Expt. 1; 2) Expt. 2.

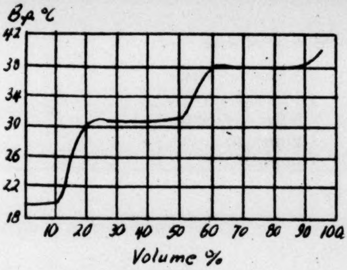

Fig. 6. Distillation curve for the product of the addition of one molecule of hydrogen to isoprene in presence of nickel.

In order to make a detailed study of the hydrogenation of isprene in presence of Raney nickel, 45.1 g of isoprene was hydrogenated. The products of the addition of one molecule of hydrogen to isoprene were treated as before, with the exception of the operation of removing isoprene with the aid of maleic anhydride, as it was considered to be absent from the mixture. It was found that there was actually a small amount of isoprene in the reaction products.

Fraction of the products of the hydrogenation of isoprene in presence of nickel (after separation from alcoholic solution) gave the results shown in Table 7 (curve in Fig. 6). In order to effect a more complete distillation of the hydrocarbons obtained, 6 ml of cyclohexane was added to the mixture to be fractionated.

Calculation of the contents of individual hydrocarbons formed by the addition of one molecule of hydrogen to isoprene in presence of nickel gave the following results:

3-Methyl-1-butene	16 mol. %
2-Methyl-1-butene	40 "
2-Methyl-2-butene	40 "
Isopentane	2 "
Isoprene	2 "

Addition of hydrogen to isoprene in presence of Raney nickel proceeds, therefore, in all possible directions. Addition proceeds mainly in the 1,4- and 3,4-positions of the conjugated system with formation of 2-methyl-2-butene and 2-methyl-1-butene respectively.

SUMMARY

1. Hydrogenation of isoprene in presence of palladium and nickel proceeds, as in the case of hydrogenation in presence of platinum studied previously by Lebedev, as a diene hydrogenation of the second type.

2. For addition of hydrogen in presence of platinum, lower selectivity is observed than in presence of palladium and nickel, which are very similar to one another in this respect.

3. The forms of the hydrogenation rate curves are in no case characteristic of the actual course of the reaction.

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REACTIONS OF INDIVIDUAL HYDROCARBONS
IN CONTACT WITH ACTIVATED TROSHKOV CLAY

COMMUNICATION 1. REACTIONS OF CYCLOHEXENE, 4-METHYLCYCLOHEXENE, AND 1-OCTENE

N. I. Shuikin and E. A. Timofeeva

The reactions of unsaturated hydrocarbons in contact with synthetic aluminosilicates have been studied in some detail [1-7]. They consist in redistribution of hydrogen (leading to formation of aromatic and saturated hydrocarbons), accompanied by reactions of dehydrocyclization, isomerization, condensation to give higher-boiling products and coke, and scission of carbon—carbon bonds; simultaneously carbonaceous deposits are formed on the catalyst. Thus, catalyzates obtained from cyclohexene in presence of aluminosilicate catalysts have been shown to contain methylcyclopentenes, methylcyclopentane, and a number of aromatic hydrocarbons, the concentration of which increased when the reaction temperature was raised; at the same time, a considerable proportion of the cyclohexene was converted into higher-boiling products and coke.

From cyclohexene at 400° in presence of an $SiO_2—Al_2O_3—ThO_2$ catalyst, Bloch and Thomas [2] obtained 97.1% of liquid catalyzate, which contained:

C_5 and C_6 alkanes	3.5%
Methylcyclopentane	26.3%
Methylcyclopentenes	23.5%
Cyclohexene	1.5%
Higher-boiling hydrocarbons (including 7% of dimethylnaphthalene)	42.2%

Greensfelder and Voge [3] studied the reactions of cyclohexene in presence of a catalyst of aluminum and zirconium silicates at 500°. They concluded that the main reactions were isomerization, saturation by hydrogen, formation of higher-boiling products and coke, and cracking.

In studies of the behavior of butenes, pentenes, hexenes, and octenes in presence of various samples of aluminosilicate catalyst it has been found that they undergo far-reaching changes: isomerization with subsequent hydrogenation of the products, partial condensation to form larger molecules, scission at carbon—carbon links, and, in some cases, conversion into aromatic hydrocarbons.

Maslyansky and Veltistova [4] heated a mixture of n-butenes at 370° in presence of a synthetic aluminosilicate catalyst and obtained, as the main product, a mixture of octenes, which was accompanied by 19% of aromatic hydrocarbons, the content of which in the catalyzate increased to almost double this value (to 37.2%) when the temperature was raised to 450°. Among the gaseous products an appreciable amount of isobutane was found.

Thomas [1] studied the reactions of octenes in presence of a catalyst of aluminum and zirconium silicates at 375°. Apart from alkenes, the catalyzate was found to contain 7-13% of aromatic hydrocarbons, 55-63% of alkanes, and 4-13% of cycloalkanes. The author pointed out that the cracking that occurs tends to lead to the preferential formation of C_3 and C_4 hydrocarbons, rather than C_1 and C_2.

Petrov and Frost [7] found that at 250° in presence of an aluminosilicate catalyst 1-octene was converted almost entirely into a mixture of octenes and octanes of branched structure, among the principal members of which were 2-methyl- and 3-methyl-heptanes.

Practically no study has been made of the behavior of individual hydrocarbons in presence of natural aluminosilicates, in spite of the fact that the latter are just as important for the treatment and purification of petroleum products as the synthetic aluminosilicates. In a previous investigation [8] we have shown that a natural aluminosilicate, activated Troshkov clay, is a good catalyst for the refinement of the middle fraction (170-300°) of the primary tar from Budagov sapropelites. At 450° and at a space velocity of 0.3, a considerable part of the unsaturated hydrocarbons of this fraction are converted into aromatics. Troshkov clay possesses also good desulfurizing properties [9].

In this investigation we decided to study the behavior of individual hydrocarbons in presence of activated Troshkov clay, and, as a result, we have determined the nature of the reactions given by cyclohexene, 4-methylcyclohexene, and 1-octene. In presence of activated Troshkov clay these hydrocarbons undergo the reactions of isomerization, hydrogenation, dehydrocyclization, condensation to products of higher molecular weight, and partial breakdown at carbon—carbon links.

EXPERIMENTAL

Original hydrocarbons. Cyclohexene and 4-methylcyclohexene were prepared by the dehydration of cyclohexanol and 4-methylcyclohexanol respectively in presence of concentrated sulfuric acid. 1-Octene was prepared by the dehydration of 1-octanol in presence of aluminum oxide at 350°. After being carefully dehydrated and distilled over sodium through a column having an efficiency of 70 theoretical plates, the hydrocarbons had the properties given in Table 1.

TABLE 1

Properties of Hydrocarbons

Hydrocarbon	B.p. (°C; corr.)	n_D^{20}	d_4^{20}	Iodine No.
Cyclohexene	82.5 - 83.5	1.4470	0.8111	311
Methylcyclohexene	102.0 - 104.0	1.4435	0.8040	264
Octene	122.5 - 124.0	1.4120	0.7170	220

The values of the constants indicate that the second hydrocarbon consisted essentially of 4-methylcyclohexene, and the third of 1-octene.

Experimental conditions and analytical procedure. The catalysis reaction was carried out in the usual flow-type apparatus at 450°, at atmospheric pressure, and with a space velocity of 0.3. The catalyst was prepared from activated Troshkov clay, activation being effected by means of sulfuric acid (the composition of the clay is given in our previous paper [8]). All the experiments were carried out with the same sample of catalyst, and the catalyst was regenerated after each experiment by passing air through it at 500° for 5-6 hours. The receiver for the catalyzate was cooled with a mixture of ice and salt, and the trap provided after the receiver was cooled with solid carbon dioxide in acetone. The gas formed was analyzed.

Refractive index, specific gravity, content of sulfonatables, and Margosches iodine number were determined for the liquid catalyzates. The adsorption method was used for the separation of the alkane—cycloalkane part of the catalyzate from the aromatic and unsaturated hydrocarbons. We found that, when the mixture under investigation contained a small amount of unsaturated hydrocarbons, these, on being adsorbed in silica gel, were to be found almost entirely in the aromatic part of the mixture. It was thus possible to separate the catalyzate into an alkane—cycloalkane part and a mixture of aromatic and unsaturated hydrocarbons.

The fractionation curves for the catalyzates and for their alkane—cycloalkane parts were obtained with the aid of a column of 70-plate efficiency, and the curves for the mixtures of aromatic and unsaturated hydrocarbons with the aid of a 20-plate column. The broken lines on the fractionation graphs indicate that in this temperature range the liquid was distilled not through the column, but from small flasks provided with Vigreux columns.

Catalytic reactions of cyclohexene. The cyclohexene was passed in portions of 50 ml (40.6 g) at a time. Two experiments were carried out, the catalyzates being united. Their properties are given in Table 2.

TABLE 2

Properties of Cyclohexene Catalyzates

Expt. No.	Amt. of catalyzate(g)	Yield of catalyzate (% by wt.)	Yield of gas (liters at STP)	n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
1	34.7	85.6	2.53	1.4700	0.8460	45.0	1.1
2	35.4	87.1	2.00	1.4690		45.0	1.2

Analysis of the Gas

Unsaturated hydrocarbons	15.9%
Hydrogen	29.9%
Paraffin hydrocarbons	54.2%

The catalyzate (55 ml, i.e. 45.5 g) was separated by adsorption on silica gel into aromatic and alkane—cycloalkane parts. The iodine number of the aromatic part was 2.5; it sulfonated completely. A formolite test on the alkane—cycloalkane part was negative. The fractionation curves for the two parts of the catalyzate are given in Fig. 1 and 2.

The alkane-cycloalkane part of the catalyzate was fractionated. The results of the fractionation and the properties of the fractions are given in Table 3.

Raman spectrum analysis, which was carried out by M. I. Batuev, showed that the first two fractions consisted essentially of methylcyclopentane, which was satisfactorily confirmed also by the properties of these fractions. On the basis of the comparatively low aniline point of Fraction III, we may suppose that this also consisted of cycloalkanes. The aromatic part of the catalyzate was separated into two fractions, the properties of which are given in Table 4.

TABLE 3

Properties of Fractions of the Alkane—Cycloalkane Part of the Cyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount		Properties		
		(g)	(% by weight)	n_D^{20}	d_4^{20}	aniline point
I	58.8 - 71.2	5.9	26.0	1.4095	0.7431	35.6
II	71.2 - 71.5	11.6	51.2	1.4088	0.7495	35.2
III	71.5 - 156.0	5.0	22.2	1.4312	0.7813	58.0
Residue	—	0.2	0.6	—	—	—

TABLE 4

Properties of Fractions of the Aromatic Part of the Cyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount		n_D^{20}
		(g)	(% by weight)	
I	110-160	3.9	19.2	1.4990
II	160-276	16.2	79.5	1.5570
Residue	—	0.3	1.3	—

Treatment of cyclohexene in contact with activated Troshkov clay as catalyst at 450° results therefore in a catalyzate containing 47% of aromatic hydrocarbons, the bulk of which boils above 160°. Benzene is not formed at all, toluene may be formed in traces, and very little of the xylenes or ethylbenzene is obtained. (See Fig. 2). In addition, 41% of methylcyclopentane was found in the catalyzate. The remaining 12% of the catalyzate was not identified, but this evidently consisted also of cycloalkanes. In the catalysis process about 14% of the original cyclohexene decomposed with formation of gaseous hydrocarbons and coke. The gas collected for analysis, consisted of 29.9% of hydrogen, 15.9% of unsaturated hydrocarbons, and 54.2% of paraffin hydrocarbons.

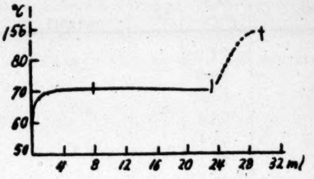


Fig. 1. Fractionation curve for the alkane—cycloalkane part of the cyclohexene catalyzate.

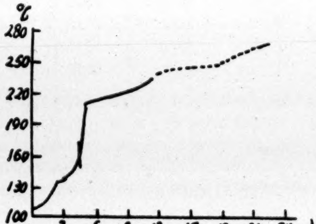


Fig. 2. Fractionation curve for the aromatic part of the cyclohexene catalyzate.

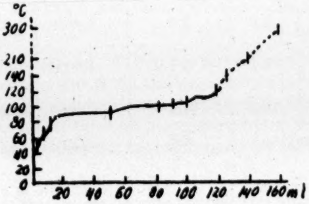
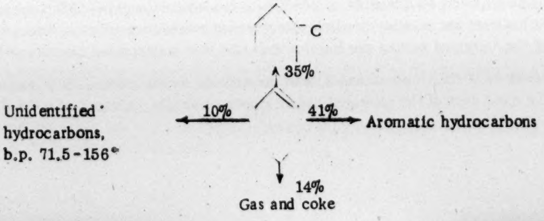


Fig. 3. Fractionation curve for the methylcyclohexene catalyzate.

The catalytic reactions of cyclohexene under the conditions of our experiments may be represented diagrammatically as follows (the percentages refer to the original hydrocarbon):



Catalytic reactions of 4-methylcyclohexene. In the first two experiments methylcyclohexene was passed in portions of 100 ml (80.4 g); in the third experiment, 120 ml (95.5 g) of this hydrocarbon was taken. The results obtained are given in Table 5.

TABLE 5

Properties of Catalyzates from 4-Methylcyclohexene

Expt. No.	Amt. of catalyzate (g)	Yield of catalyzate (% by wt.)	Yield of gas (liters STP)	n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
1	71.2	88.5	1.42	1.4550	0.8050	55.0	72.4
2	69.9	87.0	1.35	1.4530	0.8012	53.0	71.2
3	83.8	86.8	1.38	1.4535	0.8020	56.0	73.0

Analysis of the Gas

Unsaturated hydrocarbons	28.4%
Hydrogen	18.3%
Paraffin hydrocarbons	53.3%

Part of the united catalyzate (170 ml, i.e., 136.5 g) was fractionated through a 70-plate column into narrow fractions (Fig. 3). The properties of these fractions are given in Table 6.

TABLE 6

Properties of Fractions of the 4-Methylcyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount		n_D^{20}	d_4^{20}	Iodine No.	Content		
		(g)	(% by weight)				of unsat. hc. (% by wt.)	of sulfonatable hc. (% by wt.)	of aromatic hc. (% by wt.)
I	27.9-50.9	2.6	1.9	–	–	–	–	–	–
II	50.9-66.4	3.5	2.6	1.3920	0.6959	80.6	27	26	absent
III	66.4-79.1	2.8	2.1	1.4170	0.7564	82.1	31	39	8
IV	79.1-91.9	28.4	21.1	1.4109	0.7464	25.8	10	12	2
V	91.9-100.9	23.8	17.7	1.4230	0.7683	46.7	18	18	absent
VI	100.9-102.9	8.5	6.3	1.4252	0.7756	30.3	13	13	absent
VII	102.9-104.9	6.6	4.9	1.4360	0.7914	79.2	35	34	absent
VIII	104.9-122.0	17.1	12.7	1.4750	0.8405	54.1	24	89	65
IX	122.0-149.0	5.0	3.7	1.4680	0.8303	40.5	20	79	59
X	149.0-210.0	12.3	9.1	1.5025	0.8785	7.4	4	100	96
XI	210.0-302.0	19.3	14.3	1.5720	0.9646	–	absent	100	100
XII	residue	4.8	3.6	Thick resinous dark-colored liquid					

The properties of the fractions after removal of aromatic and unsaturated hydrocarbons by sulfonation are given in Table 7.

The results given in Tables 6 and 7 enable us to characterize the fraction as follows:

Fraction I, boiling range 27.9-50.9°. Very volatile mobile liquid containing unsaturated hydrocarbons. Not investigated owing to lack of material.

Fraction II, boiling range 50.9-66.4°; consisted of 26-27% of unsaturated and 74-73% of saturated hydrocarbons. It may be supposed that hexenes and possibly methylcyclopentenes entered into the composition of the unsaturated part. The properties of the saturated part of the fraction indicate that it contained isomers of hexane.

Fraction III, boiling range 66.4-79.1°; contained 31% of unsaturated hydrocarbons, 8% of benzene, and 61% of saturated hydrocarbons. The main part of the saturated hydrocarbons evidently consisted of methylcyclopentane.

Fraction IV, boiling range 79.1 - 91.9°; consisted of 10% of unsaturated hydrocarbons, 2% of benzene, and 88% of saturated hydrocarbons. After removal of aromatic and unsaturated hydrocarbons, the fraction boiled within the range 89.3 - 90.5° (through a column of 70 theoretical plates, with decane as carrier), and it could therefore be concluded that 1,3-dimethylcyclopentane was to be found in the saturated part. The aniline point and refractive index confirmed this conclusion.

Fraction V, boiling range 91.9 - 100.9°; contained 18% of unsaturated and 82% of saturated hydrocarbons. After removal of unsaturated hydrocarbons the fraction boiled over the range 92.0 - 99.0°. The boiling range, aniline point, specific gravity, and refractive index corresponded to 1,2-dimethylcyclopentane.

Fraction VI, boiling range 100.9 - 102.9°; consisted of 13.0% of unsaturated and 87.0% of saturated hydrocarbons (evidently a mixture of 1,2-dimethylcyclopentane and ethylcyclopentane).

Fraction VII, boiling range 102.9 - 104.9°; contained 35% of unsaturated and 65% of saturated hydrocarbons (judging from the properties — ethylcyclopentane).

Fraction VIII, boiling range 104.9 - 122.0°; consisted of 65% of toluene, 24% of unsaturated hydrocarbons, and 11% of cycloalkanes.

Fraction IX, boiling range 122.0 - 149.0°; contained 59% of aromatic, 20% of unsaturated, and 21% of saturated hydrocarbons.

Fraction X, boiling range 149.0 - 210°, and Fraction XI, boiling range 210 - 302°; consisted almost entirely of aromatic hydrocarbons.

TABLE 7
Properties of Fractions of the 4-Methylcyclohexene Catalyzate after the Removal of Aromatic and Unsaturated Hydrocarbons.

Fraction Number	n_D^{20}	d_4^{20}	Aniline point
II	1.3722	0.6550	74.1
III	1.4111	—	36.0
IV	1.4102	0.7480	46.2
V	1.4253	0.7718	40.9
VI	1.4227	0.7682	39.3
VII	1.4200	0.7650	38.0
VIII	1.4190	0.7708	48.7
IX	1.4285	—	—

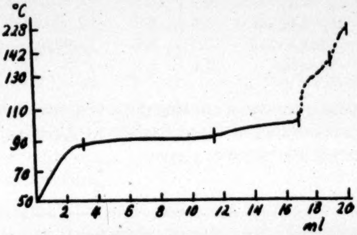


Fig. 4. Fractionation curve for the alkane—cycloalkane part of the methylcyclohexene catalyzate.

Another part of the 4-methylcyclohexene catalyzate (60 ml, i.e., 48.2 g) was passed through silica gel, isopentane being used as displacing liquid. The alkane-cycloalkane part of the catalyzate gave a negative formolite test and had an iodine number of 1.2. The whole of the mixture of aromatic and unsaturated hydrocarbons underwent sulfonation, and the iodine number of the mixture was 35.8. It may therefore be considered that the separation of the catalyzate went satisfactorily. The fractionation curves of the two parts of the catalyzate are shown in Fig. 4 and 5.

The properties of the fractions obtained from the alkane—cycloalkane part of the catalyzate are given in Table 8. The properties of the fractions isolated from the mixture of aromatic and unsaturated hydrocarbons in the catalyzate are given in Table 9.

The results given in Tables 8 and 9 confirm our conclusions concerning the composition of the saturated and aromatic hydrocarbons in the narrow fractions of the catalyzate. Fraction II (Table 8), judging by its properties, consisted almost entirely of 1,3-dimethylcyclopentane, and Fraction III — mainly of 1,2-dimethylcyclopentane.

Hence, 4-methylcyclohexene in contact with activated Troshkov clay undergoes far-reaching changes, as a result of which a catalyzate is obtained containing 38 - 40% of aromatics, 13 - 15% of unsaturated hydrocarbons, and 31% of dimethylcyclopentanes. The presence has been detected also of small amounts of hexane isomers, methylcyclopentane, and high-boiling saturated hydrocarbons, the structure of which we have not yet succeeded in establishing.

The catalytic reactions of 4-methylcyclohexene may be diagrammatically represented as follows (the percentages refer to the original hydrocarbon):

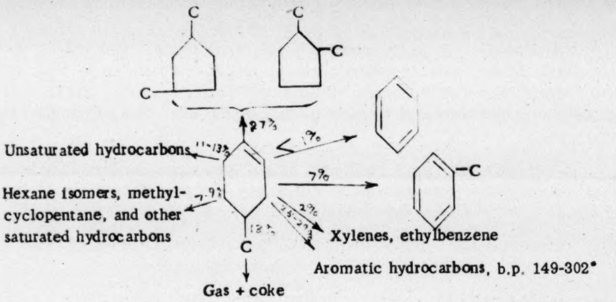

C
C
C
C
27%
Unsaturated hydrocarbons
11-13%
1%
7%
Hexane isomers, methyl-cyclopentane, and other saturated hydrocarbons
7-9%
2%
25-29%
13%
C
Xylenes, ethylbenzene
Aromatic hydrocarbons, b.p. 149-302°
Gas + coke

TABLE 8
Properties of Fractions of the Alkane-Cycloalkane Part of the 4-Methylcyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (% by wt.)	n_D^{20}	d_4^{20}	Aniline point
I	50 - 87.2	2.2	14.5	1.3892	0.7302	68.2
II	87.2 - 92.5	5.7	37.5	1.4082	0.7460	46.4
III	92.5 - 102.0	4.9	32.3	1.4155	0.7702	39.0
IV	102.0 - 142.0	1.5	9.9	1.4273	0.7722	45.0
V	142.0 - 228	0.7	4.7	1.4320	—	69.2
	Residue	0.2	1.1	—	—	—

Catalytic reactions of 1-octene. 1-Octene was passed over the same clay under the same conditions in portions of 100 ml. The results of the experiments are presented in Table 10.

The light hydrocarbons formed (boiling below 20°) were separated into three parts. The proportions by volume of these parts and their approximate compositions are given in Table 11.

Thus, 1-octene in contact with activated Troshkov clay undergoes a considerable amount of cracking (39% of gaseous hydrocarbons and coke). It was found that the approximate volume relationship of the components was $C_1 + C_2 : C_3 : C_4 = 1.3 : 3.9 : 1.6$, and 70-75% of these gases were unsaturated hydrocarbons.

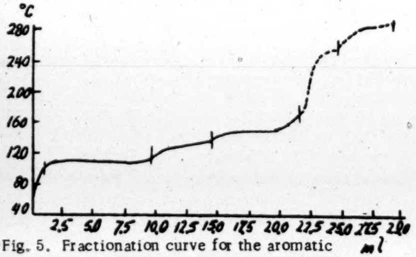


Fig. 5. Fractionation curve for the aromatic and unsaturated hydrocarbons in the methylcyclohexene catalyzate.

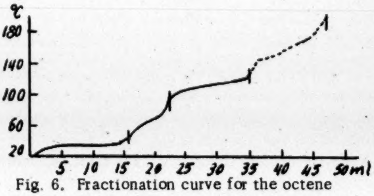


Fig. 6. Fractionation curve for the octene catalyzate.

TABLE 9
Properties of Fractions Obtained from Aromatic and Unsaturated Hydrocarbons of the 4-Methylcyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (% by weight)	n_D^{20}	d_4^{20}	Iodine No.
I	50.0 - 100.0	0.7	2.8	1.3982	—	255.0
II	100.0 - 121.0	7.5	30.1	1.4860	0.8470	63.0
III	121.0 - 148.2	4.1	16.5	1.4840	0.8460	39.5
IV	148.2 - 170.0	6.0	24.1	1.4910	0.8681	6.8
V	170.0 - 260.0	2.7	10.8	1.5210	0.8703	Unsaturated absent
VI	260.0 - 292.0	3.6	14.4	1.5640	0.8794	
	Residue	0.3	1.3	—	—	

TABLE 10

Properties of Catalyzates from 1-Octene

Expt. No.	Yield				n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
	Of liquid catalyzate		of gas condensed in trap (−60-70°)					
	(g)	(% by wt. of octene passed)	(g)	(% by wt. of octene passed)				
1	41.7	57.9	28.0	38.9	1.4100	0.7011	60.0	98.1
2	45.9	63.8	24.4	33.9	1.4115	0.7029	55.0	101.1
3	43.8	60.8	26.0	36.2	1.4160	0.7017	62.0	96.0
4	45.2	62.8	20.5	28.5	1.4135			
Mean	44.2	61.3	24.5	34.4	–	–	–	–

The united liquid catalyzate from two successive experiments (50 ml, i.e. 35.2 g) was fractionated through an efficient column into narrow fractions. Their properties are given in Table 12. The fractionation curve for the catalyzate is given in Fig. 6.

On the basis of the results given in Table 12 we may draw the following conclusions concerning the compositions of the various fractions:

Fraction I, boiling range 24.5-51.0°; consisted of a mixture of unsaturated and saturated C_6 hydrocarbons.

Fraction II, boiling range 51.0-100.0°; consisted of 32% of unsaturated C_6 and C_7 hydrocarbons, 30% aromatic hydrocarbons (mainly benzene), and 38% of saturated hydrocarbons.

Fraction III boiling range 100.0-124.0°; consisted of 26% of toluene, 11% of unsaturated, and 63% of saturated hydrocarbons.

Fraction IV, boiling range 124.0-197°; consisted mainly of aromatic hydrocarbons: it had a high refraction and a high content of sulfonatables. The content of unsaturated hydrocarbons, according to the iodine number, was 14%. The fraction, therefore, contained 81% of the aromatic hydrocarbons.

In order to make a more detailed analysis of the hydrocarbon composition, the united catalyzate from the first two experiments was separated by the adsorption method into an alkane-cycloalkane part and a mixture of aromatic and unsaturated hydrocarbons. The amount taken for the adsorption treatment was 60 ml (42.5 g). The fractionation curves of the two parts of the catalyzate are shown in Fig. 7 and 8.

TABLE 11

Composition of Gas Formed by the Cracking of 1-Octene

Expt. No.	Gas from system after trap (at −60-70°)				Gas from trap at −8°			Gas from trap and catalyzate at room temperature		
	Amount (liters at STP)	Group composition (%)			Amount (liters at STP)	Group composition (%)		Amt. (liters at STP)	Group composition (%)	
		Unsaturated hydrocarbons	Alkanes	Hydrogen		Unsaturated hydrocarbons	Alkanes		Unsat. hydrocarbons	Alkanes
1	2.70	70.8	28.0	1.2	8.11	80.0	20.0	3.2	69.2	30.8
2	2.98	65.8	30.9	3.3	7.93	68.2	31.8	2.8	81.3	18.6
3	2.23	75.9	24.1	none	7.23	75.3	24.7	3.8	73.1	26.9
4	2.62	69.0	31.0	none	7.81	72.8	27.2	3.0	72.8	27.2
Mean	2.63	70.4	28.5	1.1	7.8	74.1	25.9	3.2	74.1	25.9
Composition	–	Ethylene	Ethane, methane	Hydrogen	–	Propene	Propane	–	Butenes, isobutene	Butane, isobutane

The properties of the fractions separated from the alkane–cycloalkane part of the catalyzate are given in Table 13.

On the basis of the fractionation curve and of the properties of the fractions obtained we can state that

Fraction I consists essentially of n-pentane and isopentane; hexane, heptane and their isomers may be present in Fraction II; and in Fraction III — octane, its isomers, and hydrocarbons of more complex structure.

TABLE 12
Properties of the Fractions Obtained from the 1-Octene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (wt.%)	n_D^{20}	d_4^{20}	Sulfonatable hydrocarbons (% by wt.)	Iodine No.	Unsaturated hydrocarbons (% by wt.)	Aromatic hydrocarbons (% by wt.)	Composition of aromatic hydrocarbons
I	24.5-51.0	10.0	29.1	1.3795	0.6481	63.0	232.5	64	—	—
II	51.0-100.0	4.6	13.4	1.4175	0.7127	62.0	89.4	32	30	Mainly benzene
III	100.0-124.0	11.2	32.6	1.4295	0.7312	37.0	25.1	11	26	Mainly toluene
IV	124.0-197.0	7.7	22.4	1.4980	0.8598	95.0	24.1	14	81	Higher aromatics
	Residue	0.0	2.5	—	—	—	—	—	—	—

TABLE 13
Properties of Fractions of the Alkane–Cycloalkane Part of the 1-Octene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount % by wt	n_D^{20}	d_4^{20}	Aniline point
I	28.0- 38.2	3.4	25.0	1.3568	0.6253	—
II	38.2-100.0	2.3	17.0	1.3790	0.6610	71.7
III	100.0-146.2	7.7	56.5	1.4010	0.7162	70.8
	Residue	0.2	1.5	—	—	—

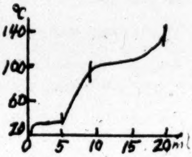


Fig. 7. Fractionation curve for the alkane-cycloalkane part of the octene catalyzate.

TABLE 14
Properties of Fractions Isolated from the Mixture of Aromatic and Unsaturated Hydrocarbons in the 1-Octene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount % by wt.	n_D^{20}	d_4^{20}
I	30 - 36.3	6.5	27.8	1.3800	0.6472
II	36.3-100.0	1.8	7.7	1.4218	0.7212
III	100.0-133.8	9.8	41.9	1.4633	0.7832
IV	133.8-190.0	5.0	21.7	1.4992	0.8611
	Residue	0.3	0.9	—	—

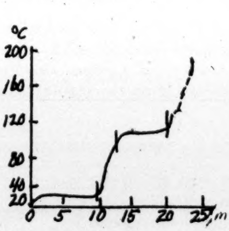
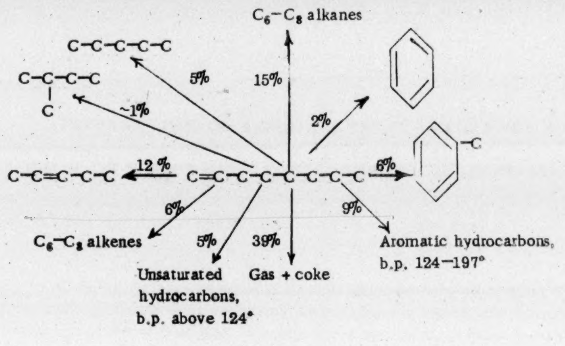


Fig. 8. Fractionation curve for the aromatic and unsaturated hydrocarbons of the octene catalyzate.

The properties of the fractions obtained from the mixture of aromatic and unsaturated hydrocarbons in the catalyzate are given in Table 14.

The fractionation curve and the properties show that Fraction I consisted mainly of 2-pentene, Fraction II evidently of hexene and heptene isomers and a small amount of benzene, Fraction III of toluene and probably of heptene and octene isomers, and Fraction IV of higher aromatics and high-boiling unsaturated hydrocarbons. Hence, the liquid catalyzate contained about 28% of aromatic hydrocarbons (including 4% of benzene, 9% of toluene, and about 15% of higher benzene homologs). The unsaturated hydrocarbons (32 - 34%) consisted of 2-pentene and evidently, also, hexene, heptene, and octene isomers, and higher-boiling hydrocarbons. The saturated part of the catalyzate consisted of n-pentane (27%), a small amount of isopentane, and probably hexane, heptane, and octane isomers.

The results, after recalculation in terms of the original 1-octene, may be presented diagrammatically as follows:



SUMMARY

1. A study has been made of the reactions of cyclohexene, 4-methylcyclohexene, and 1-octene in presence of activated Troshkov clay at 450°.

2. It has been found that the catalytic treatment leads to redistribution of hydrogen with formation of aromatic and unsaturated hydrocarbons; at the same time partial isomerization of the cyclohexenes occurs with contraction of the ring to give five-membered cycles.

3. It has been established that the formation of aromatic hydrocarbons from cyclohexenes is accompanied by alkylation reactions.

4. It has been shown that under the conditions used 1-octene undergoes dehydrocyclization with formation of aromatic hydrocarbons.

5. Under the conditions investigated, cyclohexene, 4-methylcyclohexene, and 1-octene undergo partial cracking, and some of the decomposition products of octene undergo isomerization.

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* See Consultants Bureau Translation, p. 469.

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PREPARATION OF 1,2-DIALKYLCYCLOALKANES

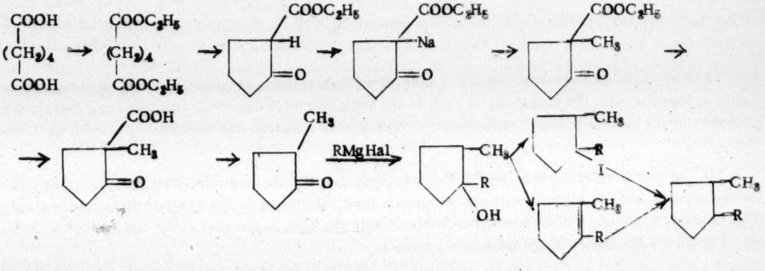
SYNTHESIS OF THE STEREOISOMERIC 1-BUTYL-2-METHYLCYCLOPENTANES

A. F. Plate, A. L. Liberman, and N. A. Momma

The preparation of dialkylcyclopentanes and dialkylcyclohexanes presents a rather difficult and laborious problem, but, since petroleum fractions contain naphthenic hydrocarbons in appreciable amount, a knowledge of the physical properties of these hydrocarbons is of great importance. In particular, in order to make a detailed study of the chemical composition of gasolines by the Raman-spectrum method [1], it is necessary to study the Raman spectra of these hydrocarbons, and for this purpose the hydrocarbons must be obtained by methods that guarantee a high degree of purity, so that they may be used as standards. However, very few methods of preparative value for obtaining dialkylcycloalkanes, particularly 1,2-dialkylcycloalkanes, are known. Thus, 1,2-dialkylcyclohexanes are generally prepared from the corresponding aromatic hydrocarbons, which are not always available in the pure state; 1-alkyl-2-methylcyclohexanes may be prepared also from 2-methylcyclohexanone. The latter method, however, suffers from the disadvantage that commercial 2-methylcyclohexanone may contain a certain amount of isomeric methylcyclohexanones, for it is generally prepared from a commercial o-cresol that is not free from other cresols.

Dialkylcyclopentanes are generally prepared from the corresponding alkylcyclopentanones. The method of preparing alkylmethylcyclopentanes proposed by Kazansky, Koperina, and Zemskaya [2] is of particular interest: they start not with individual methylcyclopentanones, but with a mixture of isomers, and the separation of the 1,2- and 1,3-isomers is carried out at the cycloalkane stage with the aid of an efficient fractionation column.

The main method for the preparation of 1,2-dialkylcyclopentanes is that used by Zelinsky and Przhevalsky [3] as long ago as 1905 for the preparation of 1,2-dimethylcyclopentane. It consists in the cyclization of diethyladipate by Bouveault's method, which yields the ethyl ester of 2-oxocyclopentanecarboxylic acid, followed by replacement of the active hydrogen atom by an alkyl group via the sodium derivative, hydrolysis, and decarboxylation. The 2-methylcyclopentanone so obtained is converted by reaction with alkylmagnesium halide into the tertiary alcohol, which is converted into the disubstituted cyclopentane in the usual way. The scheme of the reaction is as follows.



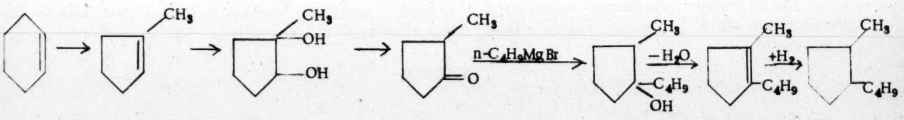
This method, in which the essential intermediate products are 2-alkylcyclopentanones, was later used to a considerable extent by Rysselberge [4] for the preparation of a number of 1,2-disubstituted cyclopentanes, and, as a result, this method is sometimes erroneously referred to in the literature as Rysselberge's method. The preparation of 2-alkylcyclopentanes by this method involves several very laborious stages, and these substances are therefore not readily accessible, in spite of a number of improvements that have been introduced into the procedure [5].

It appeared to us that a new method for the preparation of 2-methylcyclopentanone and 2-methylcyclohexanone might be found in the dehydration of secondary–tertiary diols: the dehydration of tertiary alcohol groups proceeds much more readily than that of secondary alcohol groups, and it might be expected, therefore, that in this case, the corresponding enols would be formed as intermediate products, these then rearranging into ketones. Secondary-tertiary diols can be readily obtained by oxidation under defined conditions of accessible unsaturated cyclic hydrocarbons having a methyl group on a carbon at the end of a double bond. There are indications in the literature that heating of trans-1-methyl-1,2-cyclopentanediol with sulfuric acid yields 2-methylcyclopentanone [6]. It is true that Tiffeneau and Tchoubar [7] have shown that in the dehydration of trans-1-methyl-1,2-cyclohexanediol over a heterogeneous catalyst, for which purpose they used aluminum oxide, not only 2-methylcyclohexanone, but also its isomerization product, 1-methylcyclopentanecarboxaldehyde, is formed, but it might be expected that by the use of milder conditions for the dehydration of such diols this method of obtaining cyclic α-methyl ketones could be made satisfactory for preparative purposes.

1-Methylcyclopentene, being obtainable by the isomerization of cyclohexene by Zelinsky and Arbuzov's method, is now readily accessible. This hydrocarbon was oxidized at the double bond with a mixture of hydrogen peroxide and formic acid, yielding 1-methyl-1,2-cyclopentanediol, which when dehydrated in presence of iodine yielded 2-methylcyclopentanone in 70.7 % yield, and the product formed by the loss of two molecules of water, methylcyclopentadiene, was formed simultaneously in 5% yield By the use of this method for the synthesis of 2-methylcyclopentanone it is possible to avoid a number of laborious operations and to effect a considerable economy in time, as compared with Bouveault's method.

The results obtained for the dehydration of a secondary-tertiary diol, having a six-membered ring were different from those obtained for the dehydration of a five-membered diol. Dehydration of 1-methyl-1,2-cyclohexanediol in presence of an iodine crystal gave only a 42.3% yield of 2-methylcyclohexanone, which could be isolated only by vacuum distillation through a column of 20 theoretical plates. Together with 2-methylcyclohexanone, some methylcyclohexadiene was formed, and this, in order to prove its structure, was dehydrogenated and converted into toluene. An appreciable amount of an isomerization product of 2-methylcyclohexanone was formed also; the nature of this was not established. In the case of the six-membered ring therefore, dehydration of the diol cannot be used as a preparative method for obtaining 2-methylcyclohexanone.

2-Methylcyclopentanone, prepared as indicated above, was converted by reaction with butylmagnesium bromide into a tertiary alcohol: 1-butyl-2-methylcyclopentanol. On dehydration this gave 1-butyl-2-methylcyclopentene, which on hydrogenation yielded 1-butyl-2-methylcyclopentane, previously described by Denisenko and Frolova [9]. This hydrocarbon was resolved into its previously unknown stereoisomers by vacuum fractionation through a column of 80 theoretical plates. The synthesis of the 1-butyl-2-methylcyclopentanes was therefore carried out according to the scheme:



The constants of the stereoisomeric 1-butyl-2-methylcyclopentanes obtained in this investigation are given in Table 1, together with the properties of their lower homologs – 1,2-dimethylcyclopentanes, 1-ethyl-2-methylcyclopentanes, and 1-methyl-2-propylcyclopentanes – which were prepared and separated into cis-trans isomers by Chiurdoglu [10].

Of the two stereoisomers of 1-butyl-2-methylcyclopentane that we have prepared, the isomer having the lower constants and the higher molecular refraction must, according to the Auwers–Skita rule, be assigned the trans configuration. As will be seen from Table 1, with increase in the size of the radical the difference between the constants of the trans and cis isomers diminishes.

EXPERIMENTAL

Synthesis of 2-Methylcyclopentanone and 2-Methylcyclohexanone

1-Methylcyclopentene was prepared by the isomerization of cyclohexene over aluminum oxide [8] at 450°, the space rate being 0.4 volume of liquid over 1 volume of catalyst in one hour. The dried catalyzate was fractionated through a column of 45 theoretical plates and yielded 1-methylcyclopentene having the following constants: b.p. 74.2-75.2° (760 mm); n_D^{20} 1.4325; d_4^{20} 0.7821; found MR 27.27; calculated for C_6H_{10} MR 27.24. The yield was 44-47%, calculated on the amount of cyclohexene passed, and about 54% on the amount of cyclohexene that reacted. Another isomer was obtained at the same time: 3-methylcyclopentene (b.p. 64-65° at 760 mm; n_D^{20} 1.4219, d_4^{20} 0.7654; found MR 27.26) in 15-16% yield on the amount of cyclohexene passed.

trans-1-Methyl-1,2-cyclopentanediol was obtained by the oxidation of 1-methylcyclopentene with a mixture of 30% hydrogen peroxide and 88% formic acid according to the procedure recommended for the oxidation of 1-methylcyclohexene [11], the only difference being that the temperature of the reaction mixture was maintained at 30-35°*; after removal of the solvent, the diol was distilled over under reduced pressure. Altogether, 371.2 g of 1-methyl-1,2-cyclopentanediol was obtained in the form of white crystals having the following constants: b.p. 93-95° (5 mm); m.p. 64.0-64.3°. The yield varied in different experiments from 62 to 66%. For trans-1-methyl-1,2-cyclopentanediol the literature [12] gives: b.p. 88-90° (1 mm); m.p. 65° The preparation obtained distilled over at atmospheric pressure without decomposition or dehydration: b.p. 210-211° (760 mm).

TABLE 1

Hydrocarbon	Configuration	B.p. (°C/ 760 mm)	Δt	Refractive index	Δn	d_4^{20}	Δd	Mole. refraction Found	Mole. refraction Calculated
1,2-Dimethylcyclopentane	Trans	91.78	7.4	n_{He}^{20} 1.41203	0.01027	0.75137	0.02129	32.51	
	Cis	99.23		n_{He}^{20} 1.42230		0.77266		32.31	
1-Ethyl-2-methylcyclopentane	Trans	121.4-121.75	6.3	n_D^{20} 1.4220	0.0071	0.7696	0.0150	37.02	36.94
	Cis	127.7-128.0		n_D^{20} 1.4291		0.7846		36.85	
1-Methyl-2-propylcyclopentane	Trans	146.37-146.38	6.2	n_D^{20} 1.4274	0.00692	0.7774	0.0147	41.69	41.56
	Cis	152.58		n_D^{20} 1.4343		0.7921		41.49	
1-Butyl-2-methylcyclopentane	Trans	168.9-169.0 (751 mm)	5.6	n_D^{20} 1.4321	0.0060	0.7847	0.0133	46.37	46.18
	Cis	174.5 (751 mm)		n_D^{20} 1.4381		0.7980		46.15	

2-Methylcyclopentanone was obtained by the dehydration of 1-methyl-1,2-cyclopentanediol (371.0 g), which was heated with a crystal of iodine for 30 minutes in a Favorsky flask on a Babo funnel. The ketone formed was then distilled off slowly, separated from water, washed with sodium thiosulfate solution, with sodium carbonate solution, and with water, and then dried over potassium carbonate and distilled through a column of 20 theoretical plates at 100-115 mm pressure. The results of the distillation are given in Table 2.

Fraction III was a 2-methylcyclopentanone, obtained, after the distillation through the column, in 70.7% yield. It had the following properties: b.p. 138.7° (760 mm); n_D^{20} 1.4351; d_4^{20} 0.9197; found MR 27.85; calculated for $C_6H_{10}O$ MR 27.72. For 2-methylcyclopentanone the literature [13] gives: b.p. 138.4-138.5° (742 mm); n_D^{20} 1.4350; d_4^{20} 0.9191.

In order to identify the ketone obtained, its 2,4-dinitrophenylhydrazone was prepared. It melted at 154.3-154.8°; the 2,4-dinitrohydrazone of authentic 2-methylcyclopentanone melted at 154.0-154.7°; and in admixture these substances melted at 154.3-154.8°. According to the literature [6], the 2,4-dinitrophenylhyrazone of 2-methylcyclopentanone melts at 153-154°.

Fraction I resembled cyclopentadiene in odor and was evidently methylcyclopentadiene. This fraction, on being distilled at atmospheric pressure, yielded two main fractions:

Fraction A: b.p. 73-76° (747 mm); n_D^{20} 1.444; d_4^{20} 0.8147, found MR 26.14; calculated for $C_6H_8 2\models$ MR 26.77

Fraction B: b.p. 138-160° (747 mm).

Fraction B evidently consisted mainly of a mixture of dimers of methylcyclopentadiene, whose rate of spontaneous polymerization is close to that of cyclopentadiene itself [14].

For methylcyclopentadienes of unknown structure, the literature [15] gives: b.p. 69-70° (736 mm); n_D^{18} 1.4460; d_4^{18} 0.8200; found MR 26.04; [14] b.p. 73° (760 mm); n_D^{20} 1.4509; d_4^{20} 0.8112. For the dimer of methylcyclopentadiene, the literature [14] gives: b.p. 98° (30 mm).

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* In one experiment the temperature was raised during the oxidation to 45-48° with the result that partial esterification of the diol by formic acid occurred and a mixture boiling over a wide range (80-117°/5 mm) was obtained. After hydrolysis of this mixture with 5% alcoholic caustic soda, the pure diol was isolated.

1-Methylcyclohexanol was prepared from commercial cyclohexanone (730 g) purified via the bisulfite compound, and methylmagnesium iodide, prepared from 1055 g of methyl iodide. The synthesis was carried out in batches of 2.2-2.6 moles. The decomposition of the organomagnesium complex was effected by pouring the reaction mixture onto ice. The reaction product was worked up in the usual way, and after removal of ether, the residue was distilled from a Favorsky flask, when the distillate was found to solidify in the condenser. Yields of 62-70% were obtained. Altogether 553.6 g of 1-methylcyclohexanol (66.4% yield) was obtained; it had the following constants: b.p. 55.5-56.2° (9 mm), f.p. 25.9° (from cooling curve).

For 1-methylcyclohexanol, the literature [16] gives: b.p. 56.5° (10 mm); m.p. 26°.

TABLE 2

Fraction No.	B.p. (°C; p in mm Hg)	Amount (g)
I	Up to 28 (115)	12.8
II	28.0-81.0 (115)	3.7
III	81(115), 78.4 (105)	221.5
IV	78.4-92.5 (102)	3.4
V	92.5-105.3 (103)	2.3
Residue	–	10.0
Losses	–	2.1

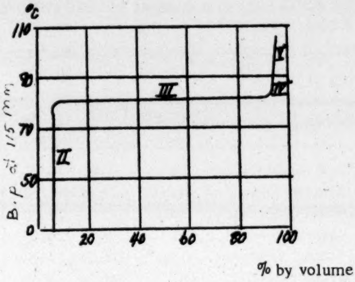

Fig. 1. Fractionation curve for 2-methylcyclopentanone

1-Methylcyclohexene was obtained by the dehydration of 1-methylcyclohexanol (519 g), which was effected by distilling it with iodine (2 g). The 1-methylcyclohexene obtained (422.7 g, 96.8%) had the following properties after being distilled through a column of 80 theoretical plates: b.p. 110.3-110.4° (760 mm); n_D^{20} 1.4510; d_4^{20} 0.8113; found MR 31.91; calculated for C_6H_{12} MR 31.86.

The data in the literature for 1-methylcyclohexene are very contradictory [17].

1-Methyl-1,2-cyclohexanediol was obtained by the oxidation of 1-methylcyclohexene (292.5 g altogether) with a mixture of 29% hydrogen peroxide and 88% formic acid [11] at 30-35°. The yield of 1-methyl-1,2-cyclohexanediol was 286 g (72%); it had b.p. 123-127° (13 mm) and m.p. 80-81°. For trans-1-methyl-1,2-cyclohexanediol the literature gives m.p. 84° [12].

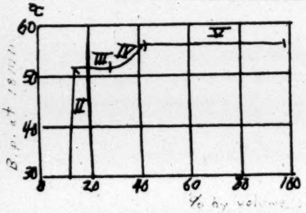

Fig. 2. Fractionation curve for dehydration product from trans-1-methyl-1,2-cyclohexanediol (fraction having b.p. 137-158° at 760 mm).

Dehydration of 1-methyl-1,2-cyclohexanediol. 1-Methyl-1,2-cyclohexanediol (282.7 g) and iodine (2.5 g) were introduced into a Favorsky flask. On being heated, the whole mass melted, and vigorous boiling then set in, water and substances not miscible with it coming over at 92-157° (measured in the vapor). The amount of water separating was 48 ml, whereas the amount calculated for the removal of one molecule of water was 39 ml. The reaction product, after being washed with sodium carbonate solution and then dried over potassium carbonate, was distilled from a Favorsky flask under atmospheric pressure. Up to 137° a fraction of 9.3 g (together with water) was collected; this was followed by 106.5 g of a fraction of b.p. 137-158°; and then decomposition set in with separation of water. The residue was vacuum-distilled, yielding a fraction which, on being redistilled, came over at 70.0-71.5° (27 mm) (62.0 g).

The fraction boiling up to 137° yielded, after being dried and redistilled, a substance having the following constants: b.p. 108-113° (745 mm); n_D^{20} 1.4713; d_4^{20} 0.8352.

This substance, on dehydrogenation in presence of platinized charcoal, yielded toluene, which was converted into 2,4-dinitrotoluene, m p. 69.0-69.7°. This preparation, in admixture with known, 2,4-dinitrotoluene, m.p. 70.2-70.5°, melted at 69.4-69.7°. Thus, the head fraction obtained in the dehydration of 1-methyl-1,2-cyclohexanediol was evidently methylcyclohexadiene, the product of the removal of two molecules of water.

The properties of 1-methyl-1,3-cyclohexadiene have not been described in the literature; 2-methyl-1,3-cyclohexadiene, according to Zelinsky and Gorsky's results [18] has the properties: b.p. 110° (741 mm); n_D^{20} 1.4710; d_4^{20} 0.8292; and according to Horiuti, Otuki, and Okuda [19]: b.p. 110 - 111° (769 mm); n_D^{20} 1.4783; d_4^{20} 0.8451.

The fraction of b.p. 137 - 158° was vacuum-distilled through a column of 20 theoretical plates. The fractionation curve is given in Fig. 2. The following fractions were collected (Table 3):

TABLE 3

Fraction No.	B.p. (°C; p in mm Hg)	Amount (g)	n_D^{20}	d_4^{20}
I	Below 31 (20.5)	9.9	1.4750	0.8415
II	31 (20.5) - 51.7 (17.5)	4.3	1.4512	0.7945
III	51.7 (17.5) - 52.0 (18)	13.6	1.4389	0.9147
IV	52.0 (18) - 56.1 (18)	13.2	1.4435	0.9151
V	56.1 (18) exactly	54.1	1.4481	0.9250
Residue	—	1.9	—	—
Losses	—	8.4	—	—

Fraction I was methylcyclohexadiene. Fraction III gave a 2,4-dinitrophenylhydrazone of m.p. 150.5 - 151°; the semicarbazone, which was obtained with difficulty and in low yield, melted at 165.4 - 166.4° (the bath was heated to 155° prior to the test). Fraction III did not decolorize bromine or cold permanganate solution, but decolorized warm permanganate solution immediately. No crystalline compound was obtained with dimedone. Schiff's reagent gave a feeble violet coloration to a layer of the organic substance The nature of this fraction has not yet been established. Fraction V gave a 2,4-dinitrophenylhydrazone of m.p. 132.0 - 133.0°. The 2,4-dinitrophenylhydrazone of known 2-methylcyclohexanone melted, without being recrystallized, at 134.5 - 135.5°, and the two preparations in admixture melted at 134.0 - 134.5°.

Analysis of 2-methylcyclohexanone-1

Found %: C 74.55; 74.59; H 10.86; 10.86

$C_7H_{12}O$. Calculated %: C 74.95; H 10.78

The fraction of the dehydration product boiling at 70.0 - 71.5° came over almost completely at exactly 56.1° (18 mm) when distilled through the column. The amount collected at this temperature was 48.8 g; there were also a fraction (5.1 g) boiling at 56.1 - 57.5° (18 mm), a residue of 5.8 g, and losses amounting to 2.3g. The fraction of b.p. 56.1° (18 mm) had n_D^{20} 1.4481; d_4^{20} 0.9250; found MR 32.47; calculated for $C_7H_{12}O$ MR 32.34. This fraction, therefore, like Fraction V of the previous fractionation, was 2-methylcyclohexanone. The total yield of this substance was 102.9 g (42.3%).

The freezing point was determined on separate batches of 2-methylcyclohexanone by the cooling-curve method. The purest batch had a freezing point of −9.15°. For 2-methylcyclohexanone the literature [20] gives: b.p. 165.08° (760 mm); m.p −14°; d_4^{20} 0.92500, [21]; n_D^{20} 1.4483.

Synthesis of 1-Butyl-2-methylcyclopentane, and its Separation into Cis and Trans Isomers

1-Butyl-2-methylcyclopentanol was prepared by the action of 2-methylcyclopentanone on butylmagnesium bromide. Owing to the fact that the ketone was not so readily accessible as butyl bromide, the latter was taken in 30% excess. The synthesis was carried out on batches of 0.5 - 1.0 mole. Altogether, 356.2 g of butyl bromide, 63.2 g of magnesium, and 196.0 g of 2-methylcyclopentanone were taken. The reaction mixture was treated in the usual way, and, after removal of ether, the reaction product was vacuum-distilled from a Favorsky flask. The results of the fractionation of one batch of the alcohol obtained are given in Table 4.

Fractions II - V were mixtures of the cis and trans isomers of 1-butyl-2-methylcyclopentanol, which explains their wide boiling ranges. An attempt to separate the stereoisomeric alcohols by distilling another batch through a column under a pressure of 6 mm was not successful: partial dehydration of the alcohol occurred. Constants were determined for two fractions of the alcohol obtained by repeated vacuum distillation:

Fraction A: b.p. 100.8° (16 mm); n_D^{20} 1.4563; d_4^{20} 0.8942; found MR 47.53.

Fraction B: b.p. 103.7 - 103.8° (16 mm); n_D^{20} 1.4576; d_4^{20} 0.8970; found MR 47.50; calculated for $C_{10}H_{20}O$ MR 47.70.

For 1-butyl-2-methylcyclopentanol (mixture of stereoisomers) the literature [9] gives: b.p. 101 - 102°

(6 mm); n_D^{20} 1.4560; d_4^{20} 0.8947; found MR 47.44.

Altogether, 148 g (54%) of 1-butyl-2-methylcyclopentanol was obtained.

1-Butyl-2-methylcyclopentene was obtained by dehydration of the alcohol in presence of iodine. The hydrocarbon obtained was distilled through a colum of 20 theoretical plates. The results of the fractionation are given in Table 5.

TABLE 4

Fraction No.	B.p. (°C; p in mm Hg)	Amount (g)	n_D^{20}
I	Up to 72 (12)	14.2	1.4362
II	72-86 (10)	17.8	1.4540
III	86-92 (12)	43.0	1.4558
IV	92-95 (13)	6.1	1.4575
V	95-98 (13)	17.0	1.4580
VI	98-108 (13)	10.0	1.4627

TABLE 5

Fraction No.	B.p. (°C; p in mm Hg)	Amount (g)	n_D^{20}
I	71.0-88.9 (45.5)	14.3	1.4501
II	88.9 (45.5); 73.3-73.5 (22)	83.7	1.4515
III	73.5-74.0 (22)	1.1	—
Residue	—	3.6	—
Losses	—	4.0	—

Fraction II was pure 1-butyl-2-methylcyclopentene. A 70% yield of pure product was obtained: b.p. 169.7-170.0° (760 mm); n_D^{20} 1.4515; d_4^{20} 0.8109; found MR 45.94; calculated for $C_{10}H_{18}$ $\overline{|}$ MR 45.71.

For 1-butyl-2-methylcyclopentene the literature [9] gives: b.p. 169.5-170.5° (752 mm); n_D^{20} 1.4480; d_4^{20} 0.8085; found MR 45.68.

1-Butyl-2-methylcyclopentane and its separation into cis and trans isomers. Hydrogenation of the cycloalkene was carried out in the cold without solvent in presence of platinized charcoal activated with palladous chloride [22]. The final purification of the 1-butyl-2-methylcyclohexane obtained was carried out by Tsvet's chromatographic adsorption method, silica gel being used as adsorbent. Altogether, 72.2 g (87%) of the hydrocarbon was obtained. In order to separate the cis and trans isomers the hydrocarbon was vacuum-distilled, using a manostat, through a column having a copper filling and of 80-plate efficiency. Two fractions were obtained, and these, on the basis of the Auwers-Skita rule, were assigned their configurations as cis and trans isomers. The yield of trans isomer (b.p. 74.0-74.1°/28 mm) was 53.3 g (74.8%), and that of the cis isomer (b.p. 78.7°/28 mm) was 14.1 g (19.8%); there was an intermediate fraction of 3.1 g (4.3%), and losses amounted to 0.8 g (1.1%). Neither a head nor a tail fraction was obtained although distillation was carried to dryness. The fractionation curve is given in Fig. 3. The boiling points of the stereoisomers at atmospheric pressure, and also their physical properties, are given above, in Table 1.

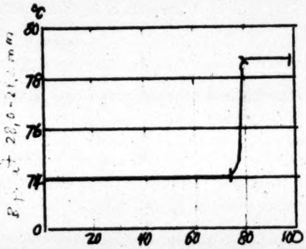

Fig. 3. Fractionation curve for 1-butyl-2-methylcyclopentane, with separation of cis and trans isomers.

Analysis of cis-1-butyl-1-methylcyclopentane:
Found %: C 85.84; 85.84; H 14.36; 14.16.

Analysis of trans-1-butyl-2-methylcyclopentane:
Found %: C 85.86; H 14.18
$C_{10}H_{20}$. Calculated %: C 85.63; H 14.37

SUMMARY

1. A suitable preparative method has been proposed for obtaining 2-methylcyclopentanone: it consists in the dehydration of the diol obtained by oxidizing 1-methylcyclopentene with a mixture of hydrogen peroxide and formic acid.

2. It has been shown that this method is of no value for the preparation of 2-methylcyclohexanone: in the case of the six-membered cycle, dehydration of the diol is accompanied by isomerization side reactions.

3. 1-Butyl-2-methylcyclopentane has been synthesized from 2-methylcyclopentanone prepared by the above method, and it has been separated into its cis and trans isomers.

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CATALYTIC OXIDATION OF THE SIMPLEST UNSATURATED HYDROCARBONS WITH HEAVY OXYGEN

L. Ya. Margolis and E. G. Plyshevskaya

A number of papers relating to the mechanism of the catalytic oxidation of hydrocarbons have recently appeared in the literature. Butyagin and Elovich [1] have established that there is a relation between the surface and space oxidation of propene in presence of platinum supported on barium sulfate. They showed that oxidation proceeds by two mechanisms: 1) purely surface, in absence of oxygen in the gas phase, and 2) surface–space. The succession of elementary processes is as follows: activated adsorption of oxygen, formation of a surface compound between propene and the oxygen of the catalyst, formation of a more highly oxidized intermediate compound, and then a fourth stage, which may proceed by the oxidation of this compound, either at the surface, giving CO_2 and H_2O, or in the space after desorption, giving CO_2 and H_2O. The authors could detect no trace of oxygen-containing products, aldehydes, and acids. Shalya, Piontkovskaya, and Polyakov [2], assert, in their paper on the mechanism of "mild" catalytic reaction, that all oxidative catalysts may yield products of partial oxidation under conditions favorable for the formation and preservation of these products. Increase in pressure and temperature leads to increase in the probability of the initiation of a homogeneous reaction at the platinum surface.

However, in numerous investigations on the oxidation of various hydrocarbons in presence of platinum catalysts [3], only traces of partial oxidation products have been detected in the reaction products: the process has always carried on to the final products, CO_2 and H_2O. Butyagin and Margolis [4], using Kovalsky's method of separation colorimetry, have established that at catalysts that produce severe oxidation (Pt, $MgCr_2O_4$) oxidation of hydrocarbons proceeds by a surface–space mechanism, but at mildly oxidative catalysts (V_2O_5, silver) a surface reaction occurs.

Thus, the principal role in the formation of products of partial oxidation is assigned by some authors to a reaction that proceeds by a surface mechanism, a sharp distinction being made between mildly and severely oxidative catalysts; whereas on the other hand, other authors explain the formation of products of partial oxidation by the presence of a space-reaction stage. The use of labeled atoms O^{18} and C^{14} will make it possible to analyze the elementary stages of the oxidation process with greater certainty and to establish their role in the formation of oxygen-containing chain molecules. The present investigation is devoted to the elucidation of the part played by the oxygen of the catalyst and of the gas phase in the oxidation of a hydrocarbon in presence of various catalysts.

EXPERIMENTAL

Procedure. Oxidation of the hydrocarbons was carried out in the previously described apparatus [5] under static conditions and at low pressure (up to 2 mm Hg). Pure ethylene and propene gases were prepared by decomposition of alcohols over active Al_2O_3, and they were purified by repeated vacuum distillation. Oxygen (O^{16}) was prepared by decomposition of twice recrystallized potassium permanganate. Heavy oxygen (O^{18}) was prepared by the electrolysis of heavy-oxygen water H_2O^{18}, containing 0.9% of O^{18}. Analysis of O^{18}-containing reaction products was carried out (as CO_2) by means of the mass spectrometer. The following were chosen as catalysts:

1) V_2O_5 (chemically pure), having a specific surface, determined by sorption of methanol, of 15 sq.m/g;

2) V_2O_4 obtained by reduction of V_2O_5, having a specific surface of 26 sq.m/g (its structure was checked by X-ray analysis: the parameters of the lattice were identical with those given in reference books);

3) $MgCr_2O_4$ (magnesium chromite), having a specific surface of 70 sq.m/g;

4) platinum supported on asbestos (2% Pt).

Oxidation of ethylene and propene. In a study of the reactions occurring in a mixture of ethylene and oxygen in presence of magnesium chromite, we have previously shown [6] that the hydrocarbon is sorbed at the surface of the catalyst, forming a stable compound, which can be removed from the surface by its further oxidation by the oxygen of the gas phase. The rate of oxidation of ethylene by the oxygen of the catalyst is considerably less than the rate of oxidation by oxygen of the gas phase.

When the balance of the reaction is analyzed, the oxidation process can be broken down into chemisorption and surface reaction. At magnesium chromite (see Table 1), as oxidation proceeds in a stoichiometric mixture of ethylene and oxygen, the proportion of the ethylene oxidized continuously falls, becoming 28% after five experiments, whereas the proportion of firmly sorbed ethylene at the surface increases from experiment to experiment, attaining the value of 66%. The surface of the catalyst is regenerated after treatment with oxygen, but the reaction products remain unchanged and consist of CO_2 and H_2O.

TABLE 1

Balance of the Oxidation Reaction in a Stoichiometric Mixture of Ethylene and Oxygen in Presence of Magnesium Chromite at 350°*

Expt. No.	Initial pressure of stoichiometric mixture**	Amount of ethylene (%)		
		Consumed in oxidation	Sorbed on surface	Residue
1	0.182	79.5	14.3	6.2
2	0.172	70.0	26.3	3.7
3	0.172	62.8	32.6	4.6
4	0.172	53.2	42.2	4.3
5	0.172	28.6	66.6	5.8
Oxygen (99 mm Hg) admitted				
6	0.163	78.0	21.0	1.0

* Duration of reaction 60 min. ** mm Hg.

TABLE 2

Balance of the Oxidation Reaction in a Stoichiometric Mixture of Ethylene and Oxygen in Presence of V_2O_5 at 430°

Expt. No.	Initial pressure of stoichiometric mixture*	Amount of ethylene (%)		
		Consumed in oxidation	Sorbed on surface	Residue
1	0.565	90.5	0.0	9.5
2	0.565	53.6	37.0	9.4
3	0.565	39.5	51.0	9.5
Treatment with oxygen				
4	0.560	67.0	25.0	8.0

* mm Hg.

Analysis of the balance of the oxidation reaction for a stoichiometric mixture of ethylene and oxygen in presence of vanadium pentoxide (see Table 2) enables us to assert that the surface of the catalyst undergoes considerable change in the course of the oxidation reaction. Thus, in the first experiment the proportion of the ethylene oxidized was 90%, but in the third it was only 9.5%. At the same time the proportion of ethylene adsorbed rose to 51%. Treatment of the catalyst surface with oxygen purified it from any compounds formed between ethylene and the oxygen of the catalyst. In Table 3 the results are given for the oxidation of the mixture $C_2H_4 + O_2$ in presence of V_2O_5 at various temperatures. With increase in temperature from 360° to 430°, the proportion of surface oxidation of C_2H_4 at the expense of the oxygen of the catalyst rose from 11 to 42%; i.e., the rate of the reaction of surface oxidation rose in comparison with the rate of oxidation by oxygen of the gas phase.

TABLE 3

Balance of the Oxidation Reaction of the Mixture $C_2H_4 + 3O_2$ in Presence of V_2O_5 at Various Temperatures*

Expt. No.	Initial pressure of mixture (mg Hg)	Temperature (°C)	Amount of oxygen (%)			Proportion of surface reaction (%)
			Used for oxidation	Adsorbed	Unused residue	
69	0.554	360	79.4	18.1	2.5	11.4
70	0.540	402	67.6	19.5	12.3	22.4
71	0.540	430	53.7	37.0	9.3	42.3

* Duration of reaction 30 min.

In the reaction products, in addition to CO_2, a large amount of CO was noted. It was established by special experiments that the appearance of carbon monoxide was associated with the decomposition of aldehydes, in presence of O_2 under static conditions at low pressure and at 350-450°, yielding carbon monoxide and hydrogen or methane.

By the amount of CO formed, therefore, an estimate can be made of the amount of aldehydes formed; i.e., of the contribution made by the partial oxidation reaction in the over-all oxidation process.

From an analysis of the balance of the reaction of stage-wise oxidation of ethylene at a V_2O_5 surface covered with oxygen, it was possible to determine the proportions of the complete- and partial-oxidation reactions, and also the contribution made by irreversible chemisorption of ethylene. It was not found possible to measure the extent of the sorption of hydrocarbons by V_2O_5, since it proceeds practically instantaneously at 250-450° and at the same time surface oxidation by the oxygen of the catalyst occurs.

TABLE 4

Balance of Stage-wise Ethylene-Oxidation Reactions on V_2O_5 at Various Temperatures*

Expt. No.	Initial pressure of C_2H_4 (mm Hg)	Temperature (°C)	Amount of ethylene (%)				CO/ CO_2 ratio
			Used in oxidation to CO_2	Used in oxidation to CO	Adsorbed	Residue	
68	0.500	360	11.3	55.2	6.5	27.7	4.9
70	0.516	402	16.3	64.0	8.4	9.7	3.9
71	0.520	430	16.7	66.2	9.0	8.1	3.9

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*Duration of reaction 90 min.

TABLE 5

Balance of Stage-wise Ethylene-oxidation Reactions on V_2O_5 at Low Pressure and Various Temperatures

Expt. No.	Initial pressure of C_2H_4 (mm Hg)	Temperature (°C)	Amount of ethylene (%)				CO/ CO_2 ratio
			Used in oxidation to CO_2	Used in oxidation to CO	Adsorbed	Residue	
68a	0.075	360	26.6	40.0	7.6	26.0	1.50
70a	0.080	402	31.5	48.7	9.0	8.7	1.54
71a	0.073	430	36.0	52.3	9.0	1.3	1.45

In Tables 4 and 5 are given the balances of the C_2H_4-oxidation reactions on V_2O_5 at various temperatures and initial pressures. With rise in temperature the proportion of unused ethylene falls, but the adsorption of ethylene on V_2O_5 is not great (6-9%). With rise in temperature the ratio CO/ CO_2 falls; i.e., the rate of the complete combustion reaction rises. In Table 5 the results are given of the oxidation of C_2H_4 on V_2O_5 at low saturations of the surface with hydrocarbon. Comparison with the results at higher pressures shows clearly that the CO/ CO_2 ratio in the reaction products falls; i.e., the proportion of the complete combustion reaction increases. The amount of oxygen on the surface and its concentration in the gas phase have, therefore, considerable effects on the direction of the oxidation reaction. In the figure, kinetic curves for the oxidation of propene on V_2O_5 and V_2O_4 are given. The rate of the oxidation of propene on V_2O_4 is considerably greater than that on V_2O_5.

Many investigators have noted [7] that for the oxidation of hydrocarbons the most active catalyst, at which a considerable amount of valuable oxygen-containing products is obtained, is V_2O_4. It has been shown in a number of investigations [8] that replacement of vanadium pentoxide by the lower oxide leads to increase in the yield of oxygen-containing products. By comparing the extents to which the oxygen of the catalyst participates in the oxidation of hydrocarbons for various catalysts, we may estimate the contributions made to the oxidative process by the surface stage, involving the oxygen of the catalyst, and by reaction at the expense of oxygen of the gas phase.

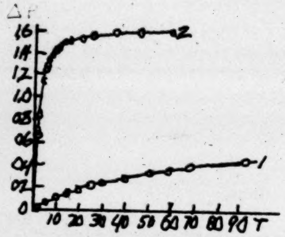
Oxidation of ethylene and propene by heavy oxygen. The study of the oxidation of hydrocarbons with the aid of the heavy oxygen isotope O^{18} was carried out by the above described procedure. Two series of experiments were carried out:

a) A stoichiometric mixture of ethylene (or propene) and heavy oxygen (O^{18}) was heated in presence of a catalyst that did not contain this isotope; and

b) O^{18} was introduced into the catalyst, and the gas mixture consisted of hydrocarbon and O^{16}-oxygen.

Results of the analysis of the reaction products on the mass spectrometer are given in Table 6. The enrichment coefficient (in $CO^{16}O^{18}$ with respect to CO_2^{16}) was determined; natural carbon dioxide CO_2^{16} provided the standard unit of measurement and the enrichment coefficient of the original O^{18}-oxygen was 1.25 relative to this standard.

If the oxidation reaction proceeded only at the expense of the oxygen in the gas phase, then the enrichment coefficient for CO_2 would be unity; but for reaction of a stoichiometric mixture of ethylene or propene with oxygen in presence of V_2O_5 containing O^{18}, the enrichment coefficient was found to be 1.19 at 350° and 1.38 at 430°. Thus both the oxygen in the gas phase and that of the catalyst took part in the oxidation of the hydrocarbon.



Kinetic curves for the oxidation of propene with oxygen at 400°:
1—on V_2O_5; 2—on V_2O_4.

TABLE 6

Oxidation of C_2H_4 and C_3H_6 with Heavy Oxygen in Presence of Various Catalysts

Expt. No.	Catalyst	Starting substances	Temperature (°C)	Enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$
2	V_2O_5 containing O^{18}	$C_2H_4 + 3O_2^{16}$	430	1.38
5	V_2O_5 not containing O^{18}	$C_2H_4 + 3O_2^{18}$	450	1.80
6	V_2O_5 not containing O^{18}	$C_2H_4 + 3O_2^{18}$	-	1.84
21	V_2O_5 containing O^{18}	$C_3H_6 + 4.5\ O_2^{16}$	350	1.19
23	V_2O_5 not containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.63
27	V_2O_5 not containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.66
24	V_2O_4 containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.81

The extent to which the oxygen of the catalyst takes part in the oxidation process may be established by carrying out the inverse experiment: reaction of a mixture of hydrocarbon and heavy oxygen in presence of a catalyst not containing O^{18}. For the oxidation of ethylene or propene in presence of vanadium pentoxide, the extent to which the oxygen of the catalyst participated in the oxidation reaction was found to be about 30%. For V_2O_4 the proportion of the surface reaction was considerably greater. Results for the reaction of various mixtures of propene and oxygen in presence of V_2O_4 containing O^{18} are given in Table 7. For the oxidation of propene adsorbed on the catalyst (only O^{16}-oxygen being present in the gas phase), the rate of the surface reaction was low. As the oxygen concentration in the gas phase was reduced, the enrichment coefficient increased; i.e., the rate of the surface reaction increased in comparison with reaction at the expense of oxygen from the gas phase.

TABLE 7

Oxidation of C_3H_6 in Presence of V_2O_4 containing O^{18} with Various Amounts of Oxygen

Expt. No.	Catalyst	Initial composition of mixture ($C_3H_6:O_2$)	Temperature (°C)	Coefficient of enrichment $CO^{18}O^{16}/CO_2^{16}$	Notes
26	V_2O_4 containing O^{18}	Only oxygen in gas phase	350	1.26	C_3H_6 adsorbed on surface of catalyst.
24	V_2O_4 containing O^{18}	1:4.5	350	1.81	
27	V_2O_4 containing O_{18}	1:1	350	2.18	CO among reaction products. Enrichment coefficient of CO 2.36.

When the oxygen concentration in the gas phase was diminished, an appreciable amount of CO appeared in the reaction products, and this provided a measure of the extent of the partial oxidation reaction. The carbon monoxide was mixed with O_2^{18} and oxidized at a platinum wire to carbon dioxide. the enrichment coefficient of which was measured by means of the mass spectrometer. The enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$ of the carbon dioxide so obtained was 2.35; i.e., the formation of carbon monoxide, and therefore of aldehydes, proceeded at the expense of the oxygen of the catalyst. In other words, the valuable oxygen-containing partial-oxidation products of hydrocarbons may be obtained in presence of those catalysts at which the rate of surface reaction is considerably greater than the rate of oxidation by oxygen from the gas phase. The enrichment coefficients of the reaction products obtained by oxidation of propene with heavy oxygen in presence of various catalysts are given in Table 8.

TABLE 8

Oxidation of C_3H_6 with Heavy Oxygen at Various Catalysts not Containing O^{18}

No.	Catalyst	Starting substances	Temperature (°C)	Enrichment coefficient $CO^{18}O^{16}/CO_2$	Proportion of surface reaction (%)
1	V_2O_4	$C_3H_6 + 4.45\ O_2^{18}$	350	1.29	42.5
2	V_2O_5	$C_3H_6 + 4.5\ O_2^{18}$	350	1.66	29.6
3	$MgCr_2O_4$	$C_3H_6 + 4.5\ O_2^{18}$	350	1.77	25.0
4	Platinum on asbestos	$C_3H_6 + 4.5\ O_2^{18}$	280	2.36	0.0

The extent to which the oxygen of the catalyst took part in the oxidation reaction varied. At V_2O_4, for example, the proportion of surface reaction was 42%; at V_2O_5 it was 30%; and at platinum at 280° oxidation proceeded only in the gas space. Hence, as we have indicated in previous papers [4], a line may be drawn between catalysts of severe and mild oxidation. The formation of partial-oxidation products is associated with reactions that proceed by a surface mechanism.

Catalysts at which the rate of surface oxidation is high are evidently the most active mild-oxidation catalysts (V_2O_4).

Reduction of the oxygen concentration in the gas phase increases the proportion of surface oxidation at the expense of the oxygen of the catalyst and favors an increase in the yield of valuable oxygen-containing products. It will be obvious that macrokinetic factors (heat, diffusion) and unfavorable relations between the rates of oxidation of the hydrocarbons and of their oxygen-containing derivatives will have a great effect on the yields of aldehydes and acids in presence of various mild-oxidation catalysts.

T. V. Bykova undergraduate, took part in the investigation. In conclusion I express my thanks to S. Z. Roginsky for valuable advice and constant interest in the work.

SUMMARY

1. A study has been made of the oxidation of ethylene and propene in presence of various catalysts (V_2O_5, V_2O_4, $MgCr_2O_4$).

2. By observations on the oxidation of ethylene and propene with heavy oxygen in presence of oxidative catalysts, the varying extents to which the oxygen of the catalyst participates in the process have been demonstrated.

3. A relation has been established between the formation of products of the partial oxidation of the hydrocarbons (aldehydes) and the extent to which the oxygen of the catalyst participates in the oxidation reaction.

4. The application of the mass spectrometer method of analysis to the reaction products from the catalytic oxidation of hydrocarbons has enabled us to explain the different mechanisms of the oxidation reactions at different catalysts.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 10. BEHAVIOR OF CYCLOHEXENE IN HYDROCONDENSATION CATALYSIS

Ya. Y. Eidus and N. I. Ershov

The catalytic hydrocondensation of carbon monoxide with olefins has been carried out only with α-olefins of the aliphatic series [1, 2]; i.e., with ethylene and its nearest homologs. propene, 1-butene, and isobutene, all of which readily undergo this reaction. It was necessary to determine the behavior in the hydrocondensation reaction with carbon monoxide of symmetrically disubstituted ethylene hydrocarbons, such as 2-butene. In order to solve this problem it was necessary to choose an olefin that could not isomerize into an α-olefin under the conditions of the reaction. Such an isomerization, with transfer of the double bond to the end of the molecule, is observed under the conditions of the oxo-synthesis reaction; i.e, the preparation of alcohols from olefins, H_2, and CO under pressure, the relevant examples being 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 2,4-dimethyl-2-pentene (as indicated by the nature of the reaction products) [3]. We chose cyclohexene, since its particular structure excludes the possibility of such isomerization. An α-olefin can be obtained from cyclohexene only by the opening of the stable six-membered ring, which is very improbable under the mild conditions of the hydrocondensation reaction (temperature, 190°; pressure, atmospheric).

EXPERIMENTAL

The apparatus and procedure were the same as in the previous investigations [1,2]. The original cyclohexene was prepared in about 80 % yield by dehydration of cyclohexanol (b.p. 158-161°/ 750 mm; d_4^{20} 0.9477) in presence of concentrated sulfuric acid by Coleman and Johnston's modification [6] of Senderens' method [7]. In Experiments 218, 219, and 221 (Tables 1 and 2) the cyclohexene used was obtained in this way, and it boiled over the range 82-84° at 763 mm and had d_4^{20} 0.8106 and n_D^{20} 1.4468. The cyclohexene used in all the remaining experiments was distilled over through a column of 40 theoretical plates, at a single point of temperature, 82.0°/ 750 mm, and it had d_4^{20} 0.8104; n_D^{20} 1.4470; found MR 27.04; calculated for C_6H_{10} = 27.19. The literature gives: d_4^{20} 83.19 at 760 mm; d_4^{20} 0.8107; n_D^{20} 1.4467 [8].

The cyclohexene passed to the glass catalysis tube (diameter 10 mm) from an automatic buret. All the experiments were performed at atmospheric pressure and at 190°. The liquid catalyzates obtained, which are described below, were dried over anhydrous copper sulfate, and the greater part of each was fractionated through a column having a metal single-helix filling, efficiency 40 theoretical plates. The residue from the fractionation was distilled from a small flask with Vigreux column (Favorsky flask).

TABLE 1

Expt. No.	Catalyst	Duration of expt. (hrs.)	Amount of cyclohexene passed		Volume of original gas (liters)	Space velocity (liters/liter-hr)			Amount of liquid catalyzate		Final volume of gas (liters)	Contraction of gas (%)
			ml	moles		cyclohexene	original gas	C_6H_{10} + gas	ml	(% of orig. C_6H_{10})		
218	46	14	111.5	1.09	0.0	0.18	–	39	109.4	98.2	–	–
219	47	16	137.8	1.35	47.0	0.25	84	138	132.0	95.8	28.7	39.0
220	48	10	115.0	1.13	33.5	0.33	95	157	112.0	97.4	17.7	47.2
221	49	20	140.5	1.39	50.2	0.20	74	120	138.2	98.4	28.25	44.0
222	48	23	230.7	2.20	66.0	0.28	82	142	229.0	99.3	34.0	48.5
223	50	27	112.4	1.07	42.9	0.12	45	71	119.6	106.5	19.7	54.1

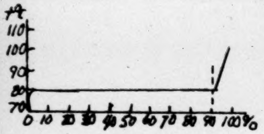


Fig. 1.

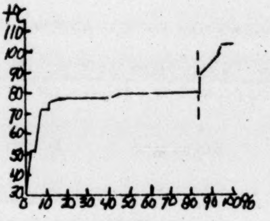


Fig. 2.

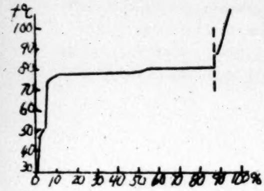


Fig. 3.

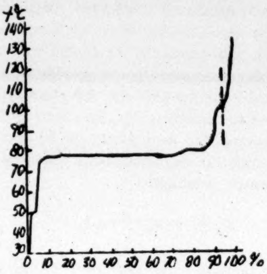


Fig 4.

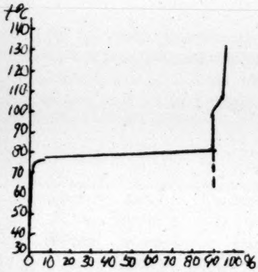


Fig. 5.

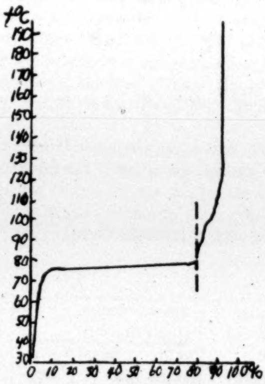


Fig. 6.

In Figures 1 – 6 the fractionation curves are given for the catalyzates, the parts on the left of the broken vertical line being the curves for fractionation through the column, and the parts on the right, fractionation curves for the residues distilled from Favorsky flasks.

Experiments with Cyclohexene without a Gas Carrier

Before investigating the behavior of cyclohexene in the reaction of hydrocondensation with carbon monoxide; i.e., before carrying out experiments with the ternary mixture $C_6H_{10} - H_2 - CO$ we studied the behavior of cyclohexene alone and also of the binary mixture $C_6H_{10} - H_2$ under similar conditions. The results obtained in the experiment on cyclohexene alone are given in Tables 1 and 2 (Expt. 218).

Cyclohexene was passed at a space velocity of 0.18 liters/liter-hour for 14 hours over freshly prepared catalyst (No. 46; weight 15.5 g, layer 44 cm in length). From 111.5 ml of hydrocarbon passed, 109.4 ml (98.2%) of liquid catalyzate was obtained; it had the constants d_4^{20} 0.8106; n_D^{20} 1.4470, which are not distinguishable from those of the original cyclohexene (see above). Distillation of 94 ml of the catalyzate through a column showed, however, that not all of the original hydrocarbon had been recovered unchanged. A fraction consisting of 91.3% by volume of the catalvzate came over in the range 71.5-82° (Fig. 1); the residue came over in the range 71.5-82° from a Favorsky flask. Details of the fractions obtained in the fractionation of the catalyzate from Expt. 218 – their volumes as percentages of the amount of catalyzate taken, their specific gravities, and their refractive indices – are given in Table 3 (intermediate fractions, comprising less than 0.2% of the original catalyzate, are not given in the table).

Experiments with Cyclohexene in a Current of Hydrogen

Two parallel experiments (Nos. 219 and 220, Tables 1 and 2) were carried out with cyclohexene passed in a current of hydrogen over freshly prepared catalyst (Nos. 47 and 48; each having weight of 15 g and layer of length 45 cm). In each pair of

TABLE 2

Expt. No.	Composition of original gas (% by volume)			Composition of original vapor phase (% by volume)				Composition of final gas (% by volume)				
	H_2	CO	C_2H_4	C_6H_{10}	H_2	CO	C_2H_4	H_2	CO	CO_2	C_nH_{2n+2}	C_nH_{2n}
218	–	–	–	100	–	–	–	–	–	–	–	–
219	100	–	–	40	60	–	–	95.0	–	–	5.0	–
220	100	–	–	43.5	56.5	–	–	Not determined				
221	88.6	11.4	–	38.3	54.7	7.0	–	75.1	–	0.9	24.0	–
222	89.4	10.6	–	42.7	51.2	6.1	–	98.8	–	–	1.2	–
223	63.9	7.0	29.1	35.8	41.0	4.5	18.7	47.7	0.2	0.5	51.3	0.3

values cited below, the first refers to Expt. No. 219 and the second to Expt. No. 220. Cyclohexene was passed for 16 (10) hours at a space velocity of 0.25 (0.33) liters/ liter-hour. The space velocity of hydrogen was 84 (95) liters/ liter-hour. The volume ratio C_6H_{10}: H_2 in the vapor-gas phase was 1: 1.5 (1: 1.3) The contraction of the hydrogen was 39.0% (47.2%). From 137.8 (115.0) ml of cyclohexene passed, 132 ml (95.8%) [112 ml (97.4%)] of liquid catalyzate was obtained.

TABLE 3
(p = 759 mm; Expt. No. 218)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	71.5-80.5	4.8	–	1.4488
II	80.5-81.5	12.0	0.8114	1.4480
III	81.5-82	74.5	0.8101	1.4465
IV	84 - 98	6.5	0.8098	1.4470
V	98 - 102	0.9	0.8110	1.4478
Residue	–	0.9	–	–
Original catalyzate	71.5 - 102	–	0.8106	1.4470

TABLE 5
(p = 750 mm; Expt. 220)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	32.5-56	4.7	0.7083	1.3960
II	73 - 77.5	8.1	0.7855	1.4340
III	77.5-78	34.6	0.7915	1.4354
IV	79 -80	40.2	0.7852	1.4300
V	86 - 108	7.4	0.7905	1.4370
Residue	–	0.5	–	–
Original catalyzate	32.5 - 108	–	0.7838	1.4320

TABLE 4
(p = 744 mm; Expt. No. 219)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	38-56	5.2	0.7199	1.3992
II	62-72	5.4	0.7831	1.4330
III	75-77	34.2	0.7988	1.4394
IV	78-79.5	13.8	0.7876	1.4296
V	79.5-80	29.9	0.7808	1.4243
VI	80-98	9.0	0.7784	1.4255
VII	99-102	4.4	0.7821	1.4285
Residue	–	0.3	–	–
Original catalyzate	38-102	–	0.7832	1.4320

The catalyzates, after being dried, had the constants d_4^{20} 0.7832, n_D^{20} 1.4340 and d_4^{20} 0.7838; n_D^{20} 1.4320. The dried catalyzates [105 ml (95 ml)] were fractionated through a column: 88.5% (87.6%) by volume of the catalyzate came over in the range 38-80° (32.5-80°) [Fig. 2 (Fig. 3)]. The residues were distilled over the range 80-102° (80°-108°) from Favorsky flasks.

The fractions, their amounts in per cent by volume, and their constants d_4^{20} and n_D^{20} are given in Tables 4 and 5.

Experiments with Cyclohexene in a Current of Hydrogen Mixed with Carbon Monoxide

Two parallel experiments were carried out also with cyclohexene; carried by a current of hydrogen mixed with carbon monoxide (Expt. No. 221 and 222, Tables 1 and 2). Expt. No. 221 was carried out with freshly prepared catalyst (No. 49; weight 15.5 g, layer 43 cm in length), whereas Expt. No. 222 was carried out with catalyst No. 48 after this had been used in Expt. No. 220. In each pair of values cited below, the first refers to Expt. No. 221, and the second to Expt. No. 222. The cyclohexene was passed for 20 (23) hours at a space velocity of 0.20 (0.28) 1/1 hr. The space velocity of the gas mixture [11.4 CO : 88.6 H_2 (10.6 CO : 89.4 H_2)] was 74 (82) 1/1 hr. The composition of the vapor phase was C_6H_{10} 38.3%, CO 7%, H_2 54.7% (C_6H_{10} 42.7%, CO 6.1%, H_2 51.2%). The total space velocity (vapor–gas phase) was 120 (142) 1/1 hr. The contraction of the gas mixture (H_2 + CO) was 44% (48.5%). The composition of the final gas was CO_2 0.9%, H_2 75.1%, CO 0.0%. C_nH_{2n+2} 24.0%, the ratio $C_2H_6:CH_4$ being 1: 10 (Podbilnyak's analysis) (CO_2 0.0%, H_2 98.8%, CO 0.0%, C_nH_{2n+2} 1.2%). From 140.5 ml (230.7 ml) of cyclohexene passed, 132 ml (98.4%) [229.0 ml (99.3%)] was obtained of catalyzate having the constants (after being dried) of d_4^{20} 0.7972; n_D^{20} 1.4413 and d_4^{20} 0.8007; n_D^{20} 1.4440. The dried catalyzate [110 ml (202 ml)] were fractionated through a column: 89.6% (93.0%) by volume of the catalyzate came over in the range 35-100° (38-81°) [Fig. 4. (Fig. 5)]. The residue was distilled from a Favorsky flask over the range 102-152° (100-133°). The fractions, their amounts in per cent by volume, and their constants are given in Table 6 (Table 7).

Experiments with Cyclohexene in a Current of Hydrogen Mixed with Carbon Monoxide and Ethylene

It was of interest to investigate the effect of additions of ethylene to the ternary mixture $C_6H_{10}-H_2-CO$. Cyclohexene was passed in a current of the mixture $H_2-CO-C_2H_4$ over freshly reduced catalyst (No. 50; weight 18 g, layer of length 45 cm) for 27 hours at a space velocity of 0.12 1/1 · hr (Expt. No. 223, Tables 1 and 2). The space velocity of the gas mixture (7 CO : 63.9 H_2: 29.1 C_2H_4) was 45 1/1 · hr, and its contraction was 54.1%. The composition of the vapor-gas phase was C_6H_{10} 35.8%, H_2 41.0%, CO 4.5%, C_2H_4 18.7%, and its space velocity was 71 1/1 · hr. The composition of the final gas was H_2 47.7%, CO 0.2%, CO_2 0.5%, C_nH_{2n} 0.3%, C_nH_{2n+2} (mainly C_2H_6) 51.3%. From 112.4 ml of cyclohexene passed, 119.6 ml (106.5%) of liquid catalyzate was obtained; after being dried it had the constants d_4^{20} 0.8003; n_D^{20} 1.4422. The dried catalyzate (100 ml) was fractionated through a column, and 80.8% by volume came over in the range 34.0-81.0° (Fig. 6). The residue was distilled from a 25-ml Favorsky flask over the range 84-150°, and the new residue from a 5-ml Wurtz flask. The fractions, their amounts in per cent by volumn, and their constants are given in Table 8.

TABLE 6

(p = 753; Expt. 221)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	35-72	5.5	0.7363	1.4011
II	73-76	8.6	0.8090	1.4514
III	77-78	52.8	0.8105	1.4504
IV	78-80	14.6	0.8137	1.4314
V	82-99	4.5	0.7756	1.4255
VI	99-100	3.6	0.7790	1.4330
VII	102-110	2.3	0.8170	1.4458
VIII	110-133	2.2	0.8028	1.4464
IX	133-152	0.4	–	–
Original catalyzate	35-152	–	0.7972	1.4413

Investigation of Reaction Products

It will be seen from Tables 1-8 and Figures 1-6 that the liquid catalyzates obtained in all of the experiments consist of three parts: 1) the higher-boiling part, 2) the middle part, represented on the fractionation curves as a plateau, and 3) the lower-boiling part.

1) Higher-boiling part of the catalyzate. The presence of Fractions IV and V (Table 3) shows that under the conditions of Expt. No. 218 products are formed that boil at a temperature higher than the boiling point of the original cyclohexene. They comprise 7.4% of the whole catalyzate and have a higher boiling limit of 102°. In Expt. No. 219-223 the products of boiling point higher than that of the original cyclohexene formed 7-14% of the catalyzate. In Expt. No. 219 and 220 with hydrogen as carrier, the upper boiling limits of the catalyzates were 102° and 108° respectively. When carbon monoxide was added (Expt. No. 219 and 220, the upper boiling limits were raised to 152° and 133° respectively, and the further addition of ethylene to the original mixture raised it to 195°. The higher-boiling products obtained from cyclohexene, CO and H_2 presented the greatest interest for investigation.

Fractions V-IX of Table 6 and Fraction VI of Table 7 were united. Part of this mixture (14 ml) having a boiling range of 95-145° and n_D^{20} 1.4390 was subjected to dehydrogenational catalysis (Zelinsky's method), two passages being given at a space velocity of 0.12 1/1 · hr in a current of hydrogen at 306-308° over a platinized charcoal catalyst prepared by Zelinsky's method [9]. The dehydrogenation catalyzate obtained had n_D^{20} 1.4862, a value that indicated a high content of aromatic hydrocarbons. Another part of the mixture (10 ml) was hydrogenated by means of two passages over the same catalyst in a current of hydrogen at 162-165°, and the catalyzate obtained had n_D^{20} 1.4239, close to the value (n_D^{20} 1.4230) for methylcyclohexane [8]. The hydrogenation catalyzate (5 ml) was now dehydrogenated over the same catalyst at 307° in a feeble current of hydrogen. The dehydrogenation catalyzate had n_D^{20} 1.4900, i.e., was strongly aromatic in character. The two dehydrogenation catalyzates (n_D^{20} 1.4862 and 1.4900) were united, and 16.5 ml of the mixture was fractionated (p = 754 mm) from a Favorsky flask into three fractions:

Fraction I, b.p. 95-105°; 4.4 ml; d_4^{20} 0.8458; n_D^{20} 1.4825

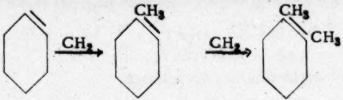
Fraction II, b.p. 105-118°; 10.2 ml; d_4^{20} 0.8516; n_D^{20} 1.4872

Fraction III, residue 1.7 ml; d_4^{20} 0.8542; n_D^{20} 1.4882

Fractions I and II gave a positive reaction for toluene when examined by Eidus and Fedichkina's test [10]. Fraction II was further fractionated, and the toluene fraction, b.p. 108-112°, was taken. A part of this (2.5 g) was subjected to Ullmann permanganate oxidation [11], and pure benzoic acid was obtained (m.p. 121.6°) with a yield of greater than 45%. In admixture with a pure preparation of benzoic acid it showed no depression in melting point.

It was thus shown that the main bulk of the higher-boiling fractions of the catalyzate obtained from the ternary mixture of cyclohexene, hydrogen, and carbon monoxide consisted of hydrocarbons having methylated six-membered rings. This indicates that methylation of cyclohexene proceeds in considerable measure under the conditions of Expt. No. 221 and 222. Fraction III (residue) (0.5 ml) was oxidized by the procedure of Norris and Vaala [12], and in the reaction product only phthalic acid could be detected (by a positive reaction, green fluorescence, with resorcinol). No isophthalic or terephthalic acid could be detected.

It has been shown, therefore, that in the hydrocondensation of cyclohexene with CO, 1,2-dimethyl-substituted products are formed according to the equation:



1,3- and 1,4-dimethyl derivatives are evidently not formed, for the methylene radical formed by reduction of CO unites with a carbon atom situated at the double bond.

2) Middle part of the catalyzate. The middle part of the catalyzate, which appears on the fractionation curves as a plateau, was found in all experiments to contain not only unchanged cyclohexene, but also cyclohexane and benzene. The middle part of the catalyzate obtained from the ternary mixture of cyclohexene, CO, and H_2 (Fractions II-V, Table 7) was investigated in the greatest detail. It was shown that these fractions consisted of hydrocarbons having a six-membered ring, as well be seen from the following experiments. A mixture of Fractions II and III (Table 7) (10 ml) was given two passages in a current of hydrogen at 160-165° over a platinized charcoal catalyst. The catalyzate, after being dried over anhydrous copper sulfate, was found to be pure cyclohexane (n_D^{20} 1.4260). For cyclohexane the literature [8] gives: b.p. 80.8°, d_4^{20} 0.77867; n_D^{20} 1.4262 [8]

TABLE 7
(p = 757; Expt. 222)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	38-56	1.5	0.7101	1.3970
II	72-75	4.8	0.7995	1.4464
III	76-78	31.5	0.8076	1.4485
IV	78.5-80	48.0	0.8036	1.4438
V	80-81	8.2	0.7955	1.4370
VI	100-133	5.0	0.8272	1.4392
Residue	–	0.4	–	–
Original catalyzate	38-133	–	0.8007	1.4440

TABLE 8
(p = 734; Expt. 223)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	34-55	3.0	0.7024	–
II	66-75	6.5	0.7817	1.4380
III	76-76.5	17.3	0.8176	1.4554
IV	76.5-79	49.0	0.8079	1.4472
V	79.5-81	5.0	0.7945	1.4362
VII	84-95	3.0	0.7873	1.4338
VIII	98-150	10.0	0.7878	1.4333
	150-195	0.8	0.8064	1.4458
Original catalyzate	34-195	–	0.8003	1.4422

The hydrogenation catalyzate (8 ml) was further subjected to dehydrogenational catalysis, being passed over the same catalyst at 306° in a feeble current of hydrogen. The dehydrogenation catalyzate obtained had n_D^{20} 1.4918. Pure cyclohexane (3 ml) passed over fresh catalyst in order to determine its activity gave a catalyzate having n_D^{20} 1.4930. In a similar way 10 ml of a mixture of Fractions IV and V (Table 7) was hydrogenated under the same conditions. The catalyzate obtained boiled at 80-81° and had n_D^{20} 1.4260, i.e. consisted of pure cyclohexane.

A mixture of Fractions II, III, IV and V (Table 7) contained a considerable amount of benzene. A qualitative test was made for benzene by the method of Eidus and Fedichkina [10]. For this purpose the mixture (10 ml) was first treated with a methanol solution of mercuric acetate in order to bind cyclohexene (which interferes in the test for benzene) in the form of its compound with the mercuric salt [14], and the unchanged residue was distilled off under reduced pressure. The distillate, containing mainly benzene and cyclohexane, gave, after partial nitration, a positive reaction for benzene with powdered KOH (under petroleum ether): a yellow coloration with alkali [10].

The same mixture of Fractions II, III, IV and V (Table 7) (n_D^{20} 1.4458) contained 33.2% by volume of cyclohexane (not absorbed by a mixture of sulfuric acid and phosphoric anhydride) and 54.3% of cyclohexene (Kaufmann bromine number of 107). The amount of benzene (by difference) was 12.5%. An artificially prepared mixture of the same composition had n_D^{20} 1.4456 and bromine number 98; 70% of its volume was absorbed by a mixture of sulfuric acid and phosphoric anhydride

Since the conditions in all of our experiments (No. 218-223) were favorable for hydrogenation and unfavorable for dehydrogenation, it must be assumed that benzene may be formed under these conditions as a result of irreversible catalysis [15, 16] according to the equation:

$$3C_6H_{10} \longrightarrow C_6H_6 + 2C_6H_{12}.$$

A comparison of the ratio of benzene and cyclohexane in the mixture of fractions (II, III, IV and V, Table 7) with that indicated in the equation leads us to assume that a part of the cyclohexene is directly hydrogenated to cyclohexane by hydrogen contained in the original gas mixture.

The presence of benzene accounts also for the apparent inconsistencies observed between the boiling points on the one hand and the values of d_4^{20} and n_D^{20} on the other in the middle fractions of the catalyzates. Actually, Fraction I (Table 3) has a somewhat higher n_D^{20} than the original cyclohexene, and Fraction II has a somewhat lower boiling point and somewhat higher values of d_4^{20} and n_D^{20} than cyclohexene.

In Tables 4 and 5 Fraction II boils lower than cyclohexene and cyclohexane, but has values of d_4^{20} and n_D^{20} that lie between those for these two hydrocarbons. The same can be said of Fraction II of Table 5. Also, Fraction III has much higher values of d_4^{20} and n_D^{20} than the following Fraction IV. In Tables 6 and 7 Fractions II and III also have values of n_D^{20} higher than that of Fraction IV. In Table 8 Fractions III, IV and V have values of d_4^{20} and n_D^{20} that rise as the boiling point of the fraction falls.

As already pointed out, all these relationships are to be explained by the presence of benzene. It was found, already in 1913 by Zelinsky and Aleksandrov [17], that benzene (b.p. 80.09° [8]) and cyclohexane (b.p. 80.8° [8]) form an azeotropic mixture boiling lower than its components (b.p. 77.5° [18], benzene content 55% by weight).

Also, benzene forms an azeotropic mixture with cyclohexene, which according to some data [18] boils at 79.8° and has a benzene content of 85% by weight, and according to other data [19] boils at 79.45° and contains 64.5% of benzene. An azeotropic mixture of benzene and cyclohexane boiling at a lower temperature than its components must therefore have higher values of the constants d_4^{20} and n_D^{20} than cyclohexene. According to Pavlov [20], a mixture of the composition indicated has d_4^{20} 0.82504 and n_D^{20} 1.46155. In the fractionation benzene naturally occurs in the lower-boiling fractions, which must therefore have higher values of d_4^{20} and n_D^{20}.

In Expt. No. 218 on cyclohexene alone, the middle part of the condensate boiled over the range 80.5-82° and comprised 86.5% by volume of the catalyzate. In Expt. No. 219-223, the middle part of the catalyzate boiled over the range 77-81° and contained cyclohexene, cyclohexane, and benzene.

3) Lower-boiling part of the catalyzate. Fraction I (Table 3), boiling range 71-80.5°, formed 4.8% of the catalyzate, and, as will be seen from Fig. 1, the part of the catalyzate boiling below 77.5° formed less than 0.5% of the catalyzate and began to boil at 71.5°. Fractions I of Tables 4 and 5, boiling ranges 38-56° and 32.5-56°, formed 5.2% and 4.7% respectively of the catalyzates. From the catalyzate of Expt. No. 219 (Table 4) an intermediate Fraction II was obtained (boiling range 62-72°, 5.4%). Fractions I of Tables 6 and 7: boiling ranges of 35-72° and 38-56° respectively; 5.5% and 1.5%. Fraction I (Table 8): 34-55°, 3%. Fraction II: 66-75°, 6.5%.

In Expt. No. 219-223, therefore, low-boiling fractions were obtained having a lower boiling limit of 32.5-38.0°. The least amount of such decomposition products was obtained in Expt. No. 222, which was carried out not with freshly reduced catalyst, but with catalyst that had been in use for a long time. These fractions were not investigated more closely, but it will be seen from their constants and boiling ranges that they contain mainly aliphatic hydrocarbons. The small steps in the fractionation curves of Fig. 2 at 49-50° and 72° are notable; also the inflexions at 49-50° in the fractionation curves of Fig. 3 and 4. These temperatures correspond to cyclopentane (b.p. 49.2° [8]) and methylcyclopentane (b.p. 71.85° [8]).

Owing to the small amounts of these intermediate fractions, we could not carry out any work on the identification of these hydrocarbons, which could have been formed by isomerization accompanied by ring contraction from six- to five-membered and then demethylation. It is very probable that these hydrocarbons will be formed. Until recently such isomerization has been observed at temperatures much higher than 190° (over V_2O_3—Al_2O_3 at 400-500° [21], Al_2O_3, TiO_2, BeO, and silica gel at 400-450° [22], Al_2O_3—Fe_2O_3 at 300° [23], clay at 260° [24], SiO_2—Al_2O_3—ThO_2 [25]). Recently, however, formation of cyclopentane attributable to the isomerization of cyclohexane into methylcyclopentane and demethylation of the latter has been observed (at 200° over a Co catalyst in preparation of synthetic gasoline [26]).

SUMMARY

1. An investigation has been made of the application of the reaction of catalytic hydrocondensation of carbon monoxide with olefins to the case of cyclohexene.

2. It has been found that under the conditions of this process "irreversible-catalysis" reactions occur with formation of benzene and cyclohexane, hydrogenation into cyclohexane occurs, and also methylation occurs with formation of 1-methyl- and 1,2-dimethyl-substituted cyclohexene.

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ORGANOMAGNESIUM SYNTHESIS OF DIBUTYL-1-NAPHTHYLPHENYLSILANE, 1-NAPHTHYLTRI-p-TOLYLSILANE, TRIBENZYL-1-NAPHTHYLSILANE, AND BENZYL-1-NAPHTHYLPHENYL-p-TOLYLSILANE

V. S. Chugunov and A. D. Petrov

In the first two communications [1] we have described methods of synthesis of sila hydrocarbons containing 1-naphthyl radicals (which we were the first to prepare) both via organomagnesium compounds and via lithium compounds. We have shown that by the organomagnesium synthesis it is possible, with tetraethoxysilane as starting material, to attach not more than two of the sterically hindering radicals 1-$C_{10}H_7$ to a silicon atom. It was established that tributyl-1-naphthylsilane and trihexyl-1-naphthylsilane are notable for their very low solidification points (of the order of −52° and −33°); also, the nonsymmetrical tetraarylsilane, 1-naphthyltriphenylsilane, melts at 183-185°, whereas tetraphenylsilane [2] melts at 234°.

Continuing these investigations, we have attempted to prepare 1-naphthyltriocytlsilane by the organomagnesium synthesis. However, under the conditions of synthesis (elevated temperature) this sila hydrocarbon was obtained only in admixture with 1-naphthyldioctylsilane. We have also prepared dibutyl-1-naphthylphenylsilane, a thick liquid having a specific gravity somewhat greater than unity and congealing to a glass at −5-7°. It has been found further that the melting point of 1-naphthyltri-p-tolylsilane (174°) is not very much lower than that of tetra-p-tolylsilane [3] (226°), and that the melting point of the isomeric tribenzyl-1-naphthylsilane is 54° (glass), which can evidently be related to the low melting point of tetrabenzylsilane [4] (127.5°). Finally, we have prepared the asymmetric sila hydrocarbon, benzyl-1-naphthylphenyl-p-tolylsilane and have found that this high-molecular-weight sila hydrocarbon, which contains five aromatic rings in its molecule, is a thick liquid at room temperature, a fact that can evidently be related to the high degree of asymmetry of its molecule.

EXPERIMENTAL

The syntheses of the sila hydrocarbons were in all cases performed via organomagnesium compounds. Decomposition of the organomagnesium complex and isolation of the final reaction products were carried out by Khotinsky and Seregenkov's method [5].

1. Dibutyl-1-naphthylphenylsilane. Diethoxy-1-naphthylphenylsilane (b.p. 365-370°; d_4^{20} 1.0552; n_D^{11} 1.5842), (20 g) and kerosene (saturated, b.p. 160-170°) (100 ml) were added to butylmagnesium chloride (0.2 mole), and the mixture, after removal of ether, was boiled in kerosene for three hours. Decomposition of the complex and fractionation of the product yielded 16.2 g of an oily liquid (b.p. 254-260°/20 mm), which, in order to remove impurities (substances containing ethoxyl groups), was again treated in kerosene at the boil with the same amount of butylmagnesium chloride After being distilled twice, dibutyl-1-naphthylphenylsilane had the following constants: b.p. 256-260°/20 mm; d_4^{20} 1.258; n_D^{20} 1.5780; yield 29% based on the 1-$C_{10}H_7C_6H_5Si(OC_2H_5)_2$ taken.

Found %: Si 8.1; 7.8

$C_{24}H_{30}Si$. Calculated %: Si 8.08

2. 1-Naphthyltrioctylsilane. Triethoxy-1-naphthylsilane (29 g) and kerosene of b.p. 160-170° (100 ml) were added to octylmagnesium bromide (0.25 mole), and after removal of ether the mixture was boiled in kerosene for four hours. Decomposition and fractionation yielded a fraction of b.p. 400-410° (14.8 g), which was again treated with excess of octylmagnesium bromide in kerosene at the boil for four hours. After two distillations a thick light-yellow oil was obtained in 27% yield; it had the following constants: b.p. 406-410°; d_4^{20} 0.9136; n_D^{20} 1.5272.

Found %:	C 82.06; 81.91;	H 11.32, 11.35;	Si 6.86, 6.78
$C_{34}H_{58}Si$. Calculated %:	C 82.65	H 11.79;	Si 5.66
$C_{26}H_{42}Si$. Calculated %:	C 81.6;	H 11 65;	Si 7.35

As the results of the elementary analysis for carbon, hydrogen, and silicon did not correspond to the compounds cited above, in spite of the fact that the contents of these elements totaled to 100%, it was suggested that the substance obtained contained not only 1-naphthyltrioctylsilane, but also a sila hydrocarbon of lower molecular weight, which, under the conditions of the synthesis, could only be 1-naphthyldioctylsilane, the presence of which we demonstrated by the method proposed by Price [6].

The mixture to be analyzed (0.4422 g) was dissolved in acetone (30 ml) in a Tserevitinov apparatus, and to this solution an equal amount of a 20% solution of caustic potash was added. The volume of hydrogen obtained was 12.4 ml, corresponding to 47.4% of 1-naphthyldioctylsilane. Treatment of 0.2014 g of the mixture gave 6.5 ml of hydrogen, corresponding to 45.2% of 1-naphthyldioctylsilane.

3. 1-Naphthyltri-p-tolylsilane. To p-tolylmagnesium bromide, prepared from 6 g of magnesium in 200 ml of ether and 69 g of p-bromotoluene, 15 g of triethoxy-1-naphthylsilane and 100 ml of saturated kerosene, b.p. 160-170°, were added. After removal of ether, the mixture was boiled in kerosene for four hours, and the complex formed was then decomposed with 50% acetic acid. Fractionation yielded 126 g of an amber-colored liquid, b.p. 320-340°/30 mm, which solidified to a glass at room temperature. In order to remove oxygen-containing compounds that were probably present as impurity, the product was again treated with an excess of p-tolylmagnesium bromide in boiling kerosene for four hours. Two vacuum fractionations yielded 9.8 g of a glasslike product, which, after two crystallizations from benzene, was obtained in the form of fine colorless crystals, m.p. 174-176°. The yield was 20%, based on the triethoxy-1-naphthylsilane taken.

Found %: C 86.60; 86.57; H 6.57; 6.73; Si 6.68; 6.67
$C_{31}H_{28}Si$. Calculated %: C 86.90; H 6.55; Si 6.55

Found M 420.2; 416.6
$C_{31}H_{28}Si$. Calculated M 428.6

4. Tribenzyl-1-naphthylsilane. To benzylmagnesium chloride (0.25 mole), prepared from 32 g of benzyl chloride and 6 g of magnesium, 14.5 g of triethoxy-1-naphthylsilane and 100 g of kerosene were added. After removal of ether, the mixture was boiled in kerosene at 160-170° for four hours, after which the complex was decomposed. A thick liquid, b.p. 310-318°/28 mm, was isolated, and this was then again treated with an excess of benzylmagnesium chloride. After decomposition of the complex, the product was vacuum-distilled twice, yielding (at 314-318°/26 mm) 4.2 g (10% of triethoxy-1-naphthylsilane taken) of tribenzyl-1-naphthylsilane, which solidified to a clear glass, softening at 54-56°. The product distilled at atmospheric pressure without decomposition at 386-389°.

Found %: C 86.68; 86.86; H 6.73; 6.51; Si 6.18; 6.36
$C_{31}H_{28}Si$. Calculated %: C 86.90; H 6.55; Si 6.55

5. Benzyl-1-naphthylphenyl-p-tolylsilane. The synthesis of this asymmetric sila hydrocarbon was performed in the following stages:

a) **Ethoxy-1-naphthylphenyl-p-tolylsilane.** To p-tolylmagnesium bromide (0.1 mole), prepared from 2.4 g of magnesium, 200 ml of ether, and 17.1 g of p-bromotoluene, 32.5 g of diethoxy-1-naphthylphenylsilane (the constants of which are given above) and 100 ml of saturated kerosene were added. After removal of ether the mixture was boiled in kerosene at 160-170° for four hours, after which the complex was decomposed and the product was vacuum-distilled twice, yielding 22 g of ethoxy-1-naphthylphenyl-p-tolylsilane, b.p. 310-318°/80 mm) and d_4^{20} 1.225, as a thick, oily liquid.

Found %: Si 7.65; 7.03
$C_{25}H_{24}SiO$. Calculated %: Si 7.69

b) **Benzyl-1-naphthylphenyl-p-tolylsilane.** Ethoxy-1-naphthylphenyl-p-tolylsilane (20 g) and kerosene of b.p. 160-170° (100 ml) were added to the product obtained from 17.1 g of benzyl chloride, 2.4 g of magnesium, and 200 g of ether. After removal of ether, the mixture was boiled in kerosene for four hours, and the product obtained by decomposing the complex was vacuum-distilled, yielding 8 g of benzyl-1-naphthylphenyl-p-tolylsilane, having the following properties: b p. 306-310°/30 mm, d_4^{20} 1.126, softening point +40-45°.

Found %: C 87.04; 87.15; H 5.96; 5.92; Si 7.4
$C_{30}H_{26}Si$. Calculated %: C 87.2; H 5.7 Si 7.0

SUMMARY

1. It has been confirmed that tetraarylsilanes of unsymmetrical structure, like their tetraarylmethane analogs, melt at lower temperatures than those of symmetrical structure.

2. It has been shown that, with increase in the chain length of the alkyl (up to C_8H_{17}) in the organomagnesium synthesis of compounds of the type $1\text{-}C_{10}H_7SiR_3$ at elevated temperatures, in addition to 1-naphtyltrioctylsilane, $1\text{-}C_{10}H_7SiH(C_8H_{17})_2$ is formed.

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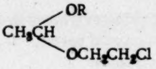
REACTIONS OF VINYL ETHERS

CHEMICAL PROPERTIES OF ALKYL 2-CHLOROETHYL ACETALS

M. F. Shostakovsky and N. A. Gershtein

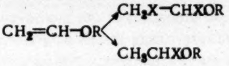
This investigation was devoted to the question of the mobility of the chlorine and hydrogen atoms occurring respectively in the 2- and 1-positions in the chloroethyl group of alkyl 2-chloroethyl acetals of general formula



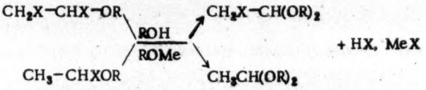
$$CH_3CH\begin{cases}OR\\OCH_2CH_2Cl\end{cases}$$

The question of the mobility of 1-halogen and 2-hydrogen has received much study in the reactions of halogen addition and hydrogen halide addition to alkyl vinyl ethers, and it has been considered in papers by Shostakovsky, Sidelkovskaya, and Bogdanova [1, 2, 3].

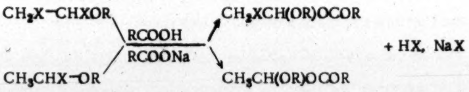
These authors have shown that 1-halogen in the products of the addition of halogen and of hydrogen halide to alkyl vinyl ethers is exceptionally mobile and is readily quantitatively titrated by the Volhard method and with alkali, and is also readily replaced by alkoxyl and acyl groups:



(I)



(II)



(III)

(X being halogen)

At the same time it was noted that 2-hydrogen was very mobile in alkyl 1,2-dihaloethyl ethers, which was shown by the tendency for hydrogen halide to be eliminated from these in presence of tertiary amines, with formation of 2-halovinyl ethers [4]:

$$CH_2X{-}CHXOR \xrightarrow{ArN(R)_2} CHX{=}CHOR \qquad (IV)$$

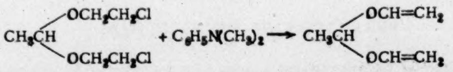
(R being alkyl)

The exceptionally high mobility of 1-halogen, and also the great readiness with which elimination and replacement reactions occur, as compared with the corresponding reactions of halogenated hydrocarbons [5], is to be attributed mainly to the effect of the ether oxygen atom, which has a free pair of electrons. Gulyaeva and Dauguleva [6] have shown, however, that in the analogous groupings of "Chlorex" $(ClCH_2CH_2)_2O$ the elimination of HCl with loss of the 2-halogen requires extremely severe conditions, divinyl ether being obtained in very low yield:

$$ClCH_2CH_2OCH_2CH_2Cl \xrightarrow[220-250^\circ]{KOH} CH_2{=}CH{-}O{-}CH{=}CH_2$$

We have now made an examination of the mobility of 2-halogen and 1-hydrogen in alkyl 2-chloroethyl acetals $[CH_3CH(OR)OCH_2CH_2Cl]$.

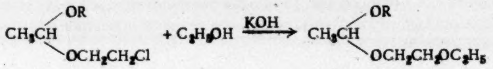
By the action of dimethylaniline on the bis(2-chloroethyl) acetal we did not, however, succeed in effecting the following reaction:



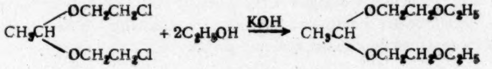
$$CH_3CH\left\langle\begin{matrix}OCH_2CH_2Cl\\OCH_2CH_2Cl\end{matrix}\right. + C_6H_5N(CH_3)_2 \rightarrow CH_3CH\left\langle\begin{matrix}OCH{=}CH_2\\OCH{=}CH_2\end{matrix}\right. \qquad (V)$$

When acetaldehyde bis(2-chloroethyl) acetal was heated at 100° for 12 hours per day for three days with an excess of dimethylaniline, there was no precipitate, and no volatile products were formed and retained in the traps, which were cooled to −50°. Under these conditions neither elimination of hydrogen chloride nor replacement of halogen by an amine group occurred. When an ether solution of the bis(2-chloroethyl) acetal was heated at a feeble boil (40°) with powdered KOH for several hours, the bis(2-chloroethyl) acetal was recovered unchanged. By heating the acetal with liquid ammonia for 5-6 hours at 140-150°, we have succeeded in replacing chlorine by the amino group [7].

The replacement of chlorine by alkoxyl in mono- and bis-2-chloroethyl acetals proceeds comparatively readily when these substances are heated with alcoholic solutions of caustic potash. The alkoxy derivatives are formed in good yield and the method may be used for preparative purposes:



$$CH_3CH\left\langle\begin{matrix}OR\\OCH_2CH_2Cl\end{matrix}\right. + C_2H_5OH \xrightarrow{KOH} CH_3CH\left\langle\begin{matrix}OR\\OCH_2CH_2OC_2H_5\end{matrix}\right. \qquad (VI)$$



$$CH_3CH\left\langle\begin{matrix}OCH_2CH_2Cl\\OCH_2CH_2Cl\end{matrix}\right. + 2C_2H_5OH \xrightarrow{KOH} CH_3CH\left\langle\begin{matrix}OCH_2CH_2OC_2H_5\\OCH_2CH_2OC_2H_5\end{matrix}\right. \qquad (VII)$$

In this communication we describe the syntheses and properties of the 2-ethoxyethyl ethyl, the butyl 2-ethoxyethyl, and the bis(2-ethoxyethyl) acetals of acetaldehyde. Only the preparation of the bis(2-ethoxyethyl) acetal is to be found in the literature: from acetaldehyde and Cellosolve by Adkins and Street [8]:

$$CH_3CHO + 2C_2H_5OCH_2CH_2OH \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2 + H_2O$$

and from acetylene and Cellosolve in presence of acid catalysts (BF_3 and HgO) by Nieuwland and coworkers [9]:

$$HC \equiv CH + 2HOCH_2CH_2OC_2H_5 \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2 .$$

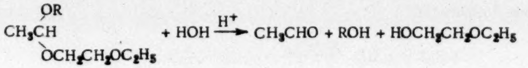
In the latter case the reaction evidently proceeds in two stages:

$$HC \equiv CH + HOCH_2CH_2OC_2H_5 \rightarrow CH_2{=}CH{-}O{-}CH_2CH_2OC_2H_5$$

$$CH_2{=}CH{-}OCH_2CH_2OC_2H_5 + HOCH_2CH_2OC_2H_5 \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2 .$$

The 2-ethoxyethyl ethyl and butyl 2-ethoxyethyl acetals were obtained for the first time by us.

The structures of the synthesized acetals were proved by hydrolysis and quantitative estimation of acetaldehyde:

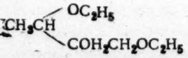


$$CH_3CH\left\langle\begin{matrix}OR\\OCH_2CH_2OC_2H_5\end{matrix}\right. + HOH \xrightarrow{H^+} CH_3CHO + ROH + HOCH_2CH_2OC_2H_5 \qquad (VIII)$$

$$CH_3CH(OCH_2CH_2OC_2H_5)_2 + HOH \xrightarrow{H^+} CH_3CHO + 2HOCH_2CH_2OC_2H_5. \qquad (IX)$$

EXPERIMENTAL*

Synthesis of the 2-Ethoxy Ethyl Acetal



$$CH_3CH\left\langle\begin{matrix}OC_2H_5\\COH_2CH_2OC_2H_5\end{matrix}\right.$$

The original 2-chloroethyl ethyl acetal was prepared by the method described previously [10] and had the following constants: b.p. 23-23.8°/2 mm; d_4^{20} 1.0190; n_D^{20} 1.4216.

A solution of caustic potash (57 g) in absolute ethanol (480 g) was introduced into a three-necked round-bottomed flask provided with mercury-sealed stirrer, reflux condenser, thermometer, and dropping funnel. Acetaldehyde 2-chloroethyl ethyl acetal (77 g) was added from the dropping funnel over a period of 2 hours 30 minutes at room temperature. No crystalline precipitate appeared in the cold, i.e., the reaction did not go at room temperature. The mixture was therefore heated with stirring at 80° for eight hours. The solution became brownish red, and a white precipitate of potassium chloride appeared. The reaction mixture was filtered under suction and then distilled from a flask fitted with a Vigreux column. It was necessary on several occasions to interrupt the distillation in order to filter off precipitated potassium chloride.

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* A. K. Gorban assisted in the experimental part.

On each occasion the precipitate of potassium chloride was washed with ether. In this way 36 g of potassium chloride (96.5% of the theoretical amount) was separated. The residue in the flask separated into layers. The lower layer was found to be an aqueous solution of caustic potash, and the upper was the reaction product, which was dried with potassium carbonate and vacuum-fractionated, yielding 9.5 g (11.7%) of the 2-ethoxyethyl ethyl acetal, b.p. 40-40.5°/4 mm, n_D^{20} 0.8955.

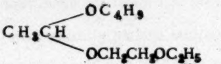
Found MR 44.33
$C_8H_{18}O_3$. Calculated MR 44.07

The substance obtained was a mobile clear liquid, very readily soluble in water, diethyl ether, ethanol, and benzene.

Found M: 148; 151.8
$C_8H_{18}O_3$. Calculated M: 162.2

Found %: C 58.61; 58.73; H 11.30; 11.18
$C_8H_{18}O_3$. Calculated %: C 59.23;
Purity %: 97.9; 99.7 (iodometrically)

Synthesis of the Butyl 2-Ethoxyethyl Acetal



$$CH_3CH\begin{cases}OC_4H_9\\OCH_2CH_2OC_2H_5\end{cases}$$

The butyl 2-chloroethyl acetal used for the reaction had b.p. 55-56°/2mm, d_4^{20} 0.9838; n_D^{20} 1.4289. A solution of 40 g of caustic potash and 118 g of absolute ethanol was placed in a three-necked round-bottomed flask provided with mercury-sealed stirrer, reflux condenser, thermometer, and dropping funnel. The reflux condenser was attached by rubber tubing to two cooling coils immersed in cooling mixture. The butyl 2-chloroethyl acetal (90 g) was added dropwise to the caustic potash solution over a period of two hours. The reaction mixture was then boiled under reflux for two hours. No evolution of gas occurred, and nothing was retained in the coils. The reaction mixture was then filtered under suction, and 32.7 g (i.e. 87.7% of the theoretical amount) of potassium chloride was separated. The filtrate was fractionated from a flask fitted with a Vigreux column. The residue in the flask separated into layers. The lower layer was an aqueous solution of caustic potash. The upper layer was dried with potassium carbonate and fractionated, yielding 91.5 g (96.2%) of the butyl 2-ethoxyethyl acetal, b.p. 71-72.5°/5 mm, d_4^{20} 0.8832; n_D^{20} 1.4090.

Found: MR 53.26
$C_{10}H_{22}O_3$. Calculated: MR 53.31

The substance obtained was a mobile, colorless liquid, soluble in diethyl ether, ethanol, and benzene.

Found %: C 63.22; 63.37; H 11.77; 11.80
$C_{10}H_{22}O_3$. Calculated %: C 63.12; H 11.65
Purity %: 99.9; 99.3 (iodometrically)

Synthesis of the Bis(2-ethoxyethyl)Acetal $CH_3CH(OCH_2CH_2OC_2H_5)_2$

Under the same conditions the bis(2-chloroethyl) acetal (b.p. 60.5-61.5°/1.5 mm; d_4^{20} 1.1737; n_D^{20} 1.4529) (47 g) was added with stirring over a period of four hours at 17-22° to a solution of 48 g of caustic potash in 414 g of absolute ethanol.

The mixture was heated in a boiling water bath for 15 hours. The solution became brown, and a white precipitate of potassium chloride formed. The reaction mixture was filtered under suction and was then distilled from a flask fitted with a Vigreux column. It was necessary to interrupt distillation on several occasions in order to filter off precipitated potassium chloride. The residue in the flask separated into layers, the lower layer being an aqueous solution of caustic potash. The upper layer was dried with potassium carbonate and then fractionated, yielding 10 g (19.3%) of the bis(2-ethoxyethyl) acetal, b.p. 109-110°/13 mm and 107-108°/10 mm, n_D^{20} 1.4181; d_4^{20} 0.9379.

Found MR 55.44
$C_{10}H_{22}O_4$. Calculated MR 54.95

According to Adkins [8]; b.p. 83-85°/10-15 mm; and according to Nieuwland[9]; b.p. 110-114°/14 mm, d_4^{25} 0.9328; n_D^{25} 1.4163.

The substance obtained was a mobile colorless liquid, soluble in benzene.

Found : M 187.8, 189.9 (cryoscopically in benzene)
$C_{10}H_{22}O_4$. Calculated: M 206.3

Found %: C 58.13; 57.99; H 10.81; 10.93
$C_{10}H_{22}O_4$. Calculated %: C 58.22; H 10.75
Purity %: 98.3; 99.0 (iodometrically)

SUMMARY

1. A method has been developed for the synthesis of alkyl 2-ethoxyethyl acetals by the action of alcoholic solutions of alkalis on alkyl 2-chloroethyl acetals.

2. By this method the 2-ethoxyethyl ethyl and the butyl 2-ethoxyethyl acetals of acetaldehyde have been prepared and fully characterized for the first time.

3. Acetaldehyde bis(2-ethoxyethyl) acetal has been synthesized by the action of alcoholic alkali on the bis(2-chloroethyl) acetal.

4. It has been shown that under the conditions studied the 2-halogen is replaced by an alkoxyl group.

5. Under the conditions studied elimination of hydrogen halide with formation of unsaturated acetals does not occur.

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* See Consultants Bureau Translation, page 1767.
** " " " " " 1367.
*** " " " " " 655.
**** " " " " " 185.

IONIC COPOLYMERIZATION OF VINYL ETHERS

M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova

The polymerization of alkyl vinyl ethers is readily brought about by the action of mineral acids and metal chlorides [1]. The dissociation of "vinyl ether —catalyst" oxonium complexes depends on the temperature, occurring approximately at the boiling point of the particular ether [1].

A study of the catalytic ionic copolymerization of ethyl vinyl and butyl vinyl ethers [2] has shown that copolymerization is preceeded by polymerization of the ethyl vinyl ether, after which a copolymer formed predominantly from units of the same ether is produced. With reduction in the amount of ethyl vinyl ether monomer in the reaction mixture, 1 : 1 copolymers are formed, or a predominance of butyl vinyl ether units may occur. Finally the polymer of butyl vinyl ether is formed.

In order to prepare copolymers from two alkyl vinyl ethers differing in activity, it is necessary to reduce the concentration of the more active monomer to a substantial extent, or to add it continuously to the reaction mixture, in which the less active monomer is in excess.

The separation of mixtures of polymers and copolymers of various compositions is based on the dissolution and extraction of the macromolecular products with various alcohols. Thus, the polymer of ethyl vinyl ether is soluble in ethanol, and the polymer of the butyl vinyl ether in butanol. Copolymers of ethyl vinyl and butyl vinyl ethers are soluble in varying degree in isopropyl alcohol (more alcohol is required for copolymers having a predominance of butyl vinyl ether units). Such copolymers are soluble also in excess of ethanol (8 —10 ml of alcohol per 1 g of copolymer). The polymer of butyl vinyl ether is soluble in butyl alcohol and is precipitated from solution by ethanol, and the polymer of ethyl vinyl ether and copolymers of ethyl vinyl and butyl vinyl ethers are precipitated from their solutions by water. By use of the method of selective dissolution and extraction of various polymerized alkyl vinyl ethers, sufficiently accurate ideas can be obtained of the course of the copolymerization of various monomers.

Ionic-copolymerization processes have been studied for the following systems, consisting of mixtures of pairs of alkyl (aryl) vinyl ethers, the alkyl (aryl) groups being: ethyl/isopropyl, ethyl/butyl, ethyl/isopentyl, ethyl/hexyl, isopropyl/butyl, butyl/heptyl, butyl/octyl, isopentyl/nonyl, isopentyl/decyl, hexyl/decyl, butyl/cyclohexyl, and butyl/phenyl.

Determinations of the refractive index of the reaction mixture were used as a check on the course of the polymerization. The course of the copolymerization process and the isolation and characterization of the products will be discussed for the example of copolymerization of ethyl vinyl and hexyl vinyl ethers.

EXPERIMENTAL

Copolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers

Expt. No. 1. Ethyl vinyl ether (b.p. 36°, n_D^{20} 1,3780); 72 g., i.e., 1 mole) and hexyl vinyl ether (b.p. 143.5°, n_D^{20} 1,4170); 128 g, i.e., 1 mole) were placed in a round-bottomed flask fitted with reflux condenser and mechanical stirrer. The mixture was warmed to 35°, and then catalyst was added (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol); the temperature then rose and the mixture thickened. The course of the copolymerization process is shown in Table 1.

The slightly yellow product, while still hot, was transferred to a Claisen flask and placed under a vacuum (15-18 mm) in a boiling water bath for two hours. The yield was 170.6 g (85%); n_D^{20} 1,4582.

a) The raw polymer was treated with three 50-ml portions of ethanol. Each extract was separately precipitated with water. Fraction I of the polymer, after being placed under vacuum (15-16 mm) in a boiling water bath for one hour had n_D^{20} 1.4486; the yield was 24 g. Fraction II had n_D^{20} 1.4490; yield 6.5 g. Fraction III had n_D^{20} 1.4503; yield 0.6 g (was not investigated further). Fractions I and II were united: total yield 30.5 g (18% on raw polymer). The isolated product was soluble in ethyl and higher alcohols, and also in ether, benzene, and acetone. It was precipitated from its solutions by water or methanol.

Found %: C 66.29, 66.23; H 11.27, 11.20

$CH_2{=}CHOC_2H_5$. Calculated %: C 66.59; H 11.18

TABLE 1

Copolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers (1: 1)

Time	n_D^{20} of mixture	Temperature of reaction mixture (°C)	Amount of catalyst
10 hrs., 40 min.	1.3975	20	–
11 " , 5 "	1.3975	35	2 drops
11 " 20 "	1.4215	65	–
11 " 35 "	1.4240	60	2 drops
11 " 50 "	1.4346	85	–
12 " 5 "	1.4380	150	2 drops
12 " 20 "	1.4425	142	–
12 " 35 "	1.4425	142.5	1 drop

According to its elementary analysis the substance appeared to be a polymer of ethyl vinyl ether.

b) The undissolved material was treated with one 100-ml portion of ethanol. After vacuum treatment as before, 12.1 g (7.0%) of a product having n_D^{20} 1.4515 was obtained. The substance was soluble in the same solvents as the polymer of ethyl vinyl ether.

Found %: C 69.13; 69.06; H 11.99; 11.77.

According to its elementary analysis the product was a copolymer of ethyl vinyl and hexyl vinyl ethers corresponding to a monomer ratio of 2 : 1.

c) The ethanol-insoluble raw polymer was treated with 50 ml of a 1 : 1 mixture of hexyl and ethyl alcohols. from the extract 10.3 g (6.0% on the raw polymer) of a product having n_D^{20} 1.4528 was obtained.

Found %: C 70.37; 70.16; H 11.83; 11.99.

The analytical results indicate a copolymer having a monomer ratio of 5 : 4.

d) The raw polymer was treated twice with fresh 100-ml portions of a 1 : 1 mixture of ethyl and hexyl alcohols. The products isolated were found to be close with respect to refractive index (1.4557 and 1.4560), and they were united. The yield was 73.2 g (43%); n_D^{20} 1.4558.

Found %: C 71.73; 71.59; H 12.14; 12.18

CH_2=$CHOC_2H_5$ + CH_2=$CHOC_6H_{13}$. Calculated %: C 72; H 12

e) The residual raw polymer (2 g, n_D^{20} 1.4600), which was insoluble in the mixture of ethyl and hexyl alcohols, dissolved completely in hexyl alcohol. It was not investigated further.

The total yield of polymers and copolymers was 128.7 g (75.4% on the raw polymer).

Expt. No. 2. Ethyl vinyl ether (36 g, i.e., 0.5 mole) and hexyl vinyl ether (128 g, i.e., 1 mole) were placed in the flask (the apparatus and the constants of the ethers were the same as in Expt. No. 1). The course of the copolymerization is shown in Table 2.

TABLE 2

Copolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers (1:2)

Time	n_D^{20} of mixture	Temperature of reaction mixture (°C)	Amount of catalyst (drops)
10 hrs. 10 min.	1.4040	21	–
10 " 30 "	1.4040	35	2
10 " 45 "	1.4270	72	–
11 " 0 "	1.4285	67	2
11 " 15 "	1.4377	123	–
11 " 30 "	1.4400	124	2
11 " 45 "	1.4486	148	–
12 " 0 "	1.4490	144	1
12 " 15 "	1.4492	145	–

After vacuum treatment under the conditions of Expt. No. 1, 141.6 g (86.8%) of substance, n_D^{20} 1.4605, was obtained.

a) The raw polymer was treated with 100 ml of ethanol. The polymer that dissolved in the ethanol was precipitated with water. Solvent was driven off, and the product was placed under vacuum in a boiling water bath for about one hour. The yield was 10.0 g (7% on the raw polymer); n_D^{20} 1.4518.

Found %: C 69.58; 69.35; H 12.00; 11.82

The copolymer, according to its elementary analysis, refractive index, and solubility, corresponded to that described in Expt. No. 1 b.

b) The ethanol-insoluble raw polymer was treated with 50 ml of a mixture of ethyl and hexyl alcohols (1 : 1). From the extract 17.2 g (12%) of a product of n_D^{20} 1.4525 was obtained.

Found %: C 70.64; 70.52; H 11.78; 12.02.

This copolymer, according to its elementary analysis, was close to that described in Expt. No 1c.

c) The raw polymer was treated with two 150-ml portions of a 1 : 1 mixture of ethyl and hexyl alcohols. From the extract 37.6 g (27%) of a product of n_D^{20} 1.4563 was obtained. It corresponded in its properties to the copolymer described in Expt. No. 1d.

d) The raw polymer was treated with 75 ml of the same solvent (c). From the extract 2.8 g (2%) of a product of n_D^{20} 1.4568 was obtained.

Found %: C 71.13, 71.05; H 11.79; 11.92.

TABLE 3

Characteristics of Copolymers of Vinyl Ethers

Composition of Copolymer	Yield (%)	d_4^{20}	n_D^{20}	Absolute viscosity of a 0.1 M benzene solution at 20° (centipoise)	Molecular weight found	Degree of polymerization	Found		Solubility
							% C	% H	
$[CH_2{=}CHOC_2H_5 + CH_2{=}CHOCH(CH_3)_2]_n$	52	0.9270	1.4510	0.7867	4295	54	68.15	11.27	Soluble in ethyl and higher alcohols, ether, benzene, acetone
$[CH_2{=}CHOC_2H_5 + CH_2{=}CHOC_4H_9]_n$	54	0.9245	1.4530	0.7349	2150	25	70.16	11.99	"
$[CH_2{=}CHOC_2H_5 + CH_2{=}CHOCH_2CH_2CH(CH_3)_2]_n$	48	0.9244	1.4542	0.6885	1691	18	69.86	11.45	"
$[CH_2{=}CHOC_2H_5 + CH_2{=}CHOC_6H_{13}]_n$	43	0.9233	1.4558	0.8054	3919	39	71.73	12.14	"
$[CH_2{=}CHOCH(CH_3)_2 + CH_2{=}CHOC_4H_9]_n$	75	0.9230	1.4545	0.7330	2084	22	70.71	11.21	Soluble in propyl and higher alcohols, ether, benzene, acetone
$[CH_2{=}CHOC_4H_9 + CH_2{=}CHOC_7H_{15}]_n$	79	0.9260	1.4590	0.8662	4642	38	73.98	12.44	Soluble in butyl and higher alcohols, ether, benzene, acetone
$[CH_2{=}CHOC_4H_9 + CH_2{=}CHOC_8H_{17}]_n$	76	0.9243	1.4620	0.9595	7034	55	74.14	12.56	"
$[CH_2{=}CHOCH_2CH_2CH(CH_3)_2 + CH{=}CHOC_9H_{19}]_n$	50	0.9198	1.4623	0.8311	3262	23	75.59	12.65	Soluble in isopentyl and higher alcohols, ether, benzene, acetone
$[CH_2{=}CHOCH_2CH_2CH_2CH(CH_3)_2 + CH_2{=}CHOC_{10}H_{21}]_n$	51	0.9217	1.4670	0.8464	3482	23	75.86	12.75	"
$[CH_2{=}CHOC_6H_{13} + CH_2{=}CHOC_{10}H_{21}]_n$	59	0.9231	1.4657	0.8807	4710	30	76.38	12.90	Soluble in hexyl and higher alcohols, ether, benzene
$[CH_2{=}CHOC_4H_9 + CH_2{=}CHOC_6H_{11}]_n$	62	0.9316	1.4800	0.8618	4125	36	74.23	11.59	Soluble in butyl alcohol, ether, benzene
$[CH{=}CHOC_4H_9 + CH_2{=}CHOC_6H_5]_n$	49	0.9620	1.5070	0.7312	1661	15	75.99	9.17	

The analytical results indicate a copolymer having a monomer ratio of 4 : 5.

e) Raw polymer insoluble in the alcohol mixture was completely soluble in 150 ml of hexyl alcohol, and was precipitated from solution by 200 ml of ethanol. After removal of solvents by distillation and vacuum treatment to constant weight, the yield of product was 46.3 g (33%); n_D^{20} 1.4633. According to its properties the product was a polymer of hexyl vinyl ether.

Found %: C 74.79; 74.89; H 12.59; 12.38

p-$C_6H_{13}OCH{=}CH_2$. Calculated %: C 74.94; H 12.59

The total yield of polymers and copolymers was 113.9 g (81% on the raw polymer).

The properties of copolymers in which the original monomers occur in the ratio of 1 : 1 are given in Table 3.

In order to verify the accuracy of the method of selective separation of polymers, polymerized ethyl vinyl ether (n_D^{20} 1.4518) and polymerized hexyl vinyl ether (n_D^{20} 1.4630) (50 g of each) were taken and mixed carefully. The homogeneous mixture was first treated with three 80-ml portions of ethanol, polymer being then precipitated with water. From the first extract 24 g of polymerized ethyl vinyl ether was obtained, from the second 16.5 g, and from the third 2 g. The total yield of polymerized ethyl vinyl ether was 42 g (84%); n_D^{20} 1.4515 – 1.4520. The ethanol-insoluble polymer dissolved completely in 140 ml of hexyl alcohol and was reprecipitated with 250 ml of ethanol. The yield of polymerized hexyl vinyl ether was 46 g (92%); n_D^{20} 1.4635.

SUMMARY

1. A study has been made of the copolymerization of alkyl (C_4–C_{12}) vinyl ethers.

2. The copolymers obtained have been characterized by elementary analysis, solubility, viscosity, and molecular weight determinations.

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of the USSR Academy of Sciences

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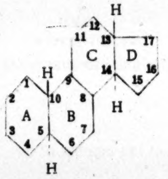
NOMENCLATURE OF SYNTHETIC STEROIDS AND RELATED SUBSTANCES*

I. N. Nazarov

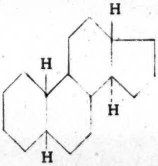
During the last seven years extensive and systematic investigations have been proceeding in our laboratory on the synthesis of steroid compounds and related substances. These investigations have led to the synthesis of numerous polycyclic compounds derived from hydrogenated cyclopentaphenanthrene, chrysene, benzofluorene, and their heterocyclic (sulfur) analogs. With the appearance of these compounds an urgent need arose for the development of a general system of nomenclature that would cover not only the synthetic steroids known at present, but would be suitable for the description of any new steroid compounds and related substances, which will no doubt appear in the future in ever increasing number.

The nomenclature recently adopted at a London conference [1] for steroids is applicable only to natural products and is intended for the description of steroids of any one strictly defined spatial configuration. This nomenclature does not permit the description of synthetic steroid compounds that are distinct from the natural steroids and must often be dealt with in the performance of a complete synthesis.

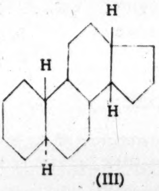
For the description of synthetic steroid compounds, irrespective of their optical activity or membership of a particular series of natural steroids and taking into account only the spatial structure of the steroid skeleton, we propose the following eight names for the fundamental hydrocarbons of the perhydrocyclopenta[a]phenanthrene series and the perhydrochrysene series:



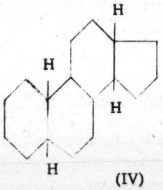
(I)
Allosterane



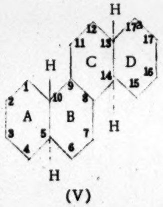
(II)
Sterane



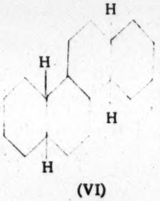
(III)
Allocardosterane
(Allisosterane)



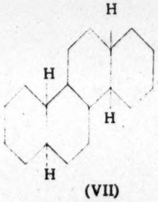
(IV)
Cardosterane
(Isosterane)



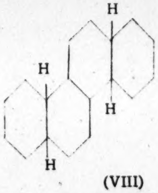
(V)
Allochrysane
D-Homoallosterane)



(VI)
Chrysane
(D-Homosterane)



(VII)
Allocardochrysane
(D-Homoallocardo-
sterane)

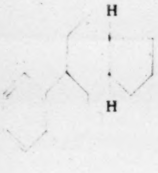


(VIII)
Cardochrysane
(D-Homocardo-
sterane)

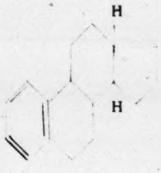
---

* In view of the nature of this article, the names of compounds have been transcribed as directly as possible. American practice, however, has been followed for indicating positions of double bonds ($\Delta^{9:11}$, etc. is used in the original). The Russian ending –an has been transcribed as –ane for fully saturated compounds, and in other cases as –an. (Publisher.)

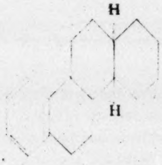
The fundamental steroid hydrocarbons containing one aromatic ring A or two aromatic rings A and B, which form the basis for the estrogenic hormones of the estrone and equilenin groups, receive the following names:



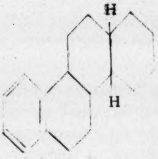
(IX)
Estrosteran



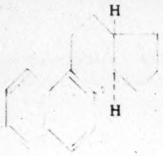
(X)
Isoestrosteran



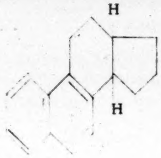
(XI)
Estrochrysan
(D-Homoestrosteran)



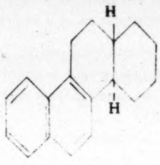
(XII)
Isoestrochrysan
(D-Homoestrosteran)



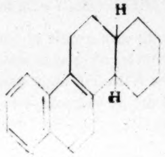
(XIII)
Equisteran



(XIV)
Isoequisteran



(XV)
Equichrysan
(D-Homoequisteran)

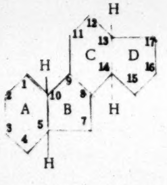


(XVI)
Isoequichrysan
(D-Homoisoequisteran)

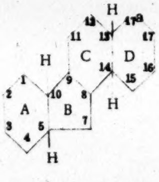
Ring Enlargement and Contraction

When ring enlargement occurs, the extra atom of the homosteroid compound preserves the number of the preceding carbon atom with addition of the letter "a" (see Formulas V and XVIII).

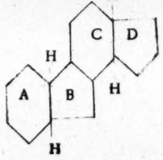
When ring contraction occurs, a carbon atom is removed, and all the remaining atoms in the norsteroid compound retain their usual numbers (see Formulas XVII and XVIII):


H
12
11
13
17
C
D
14
16
15
H
1
9
2
10
8
A
B
H
7
3
5
4
H

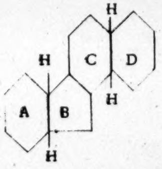
(XVII)
B-Norsterane


H
12
13
17a
11
17
H
C
D
14
16
15
1
9
2
10
8
A
B
H
7
3
5
4
H

(XVIII)
B-Norchrysane



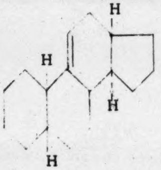
(XIX)
B-Norcardosterane



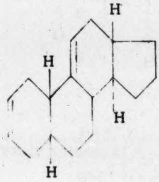
(XX)
B-Norcardochrysane

Indication of Double Bonds

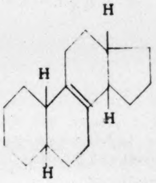
Double bonds are indicated in the usual way, except in the case of the chrysane hydrocarbons, the introduction of one double bond into which is indicated by the addition of the suffix -ene to the name of the hydrocarbon itself (see Formulas XXIV and XXVI):



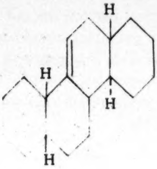
(XXI)
9(11)-Sterene



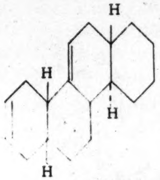
(XXII)
2,9(11)-Steradiene



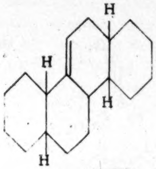
(XXIII)
8(9)-Cardosterene



(XXIV)
9(11)-Chrysanene



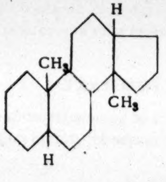
(XXV)
2,9(11)-Chrysadiene



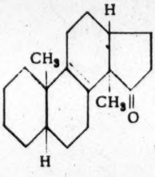
(XXVI)
9(11)-Cardochrysanene

Indication of Substituents and Functional Groups

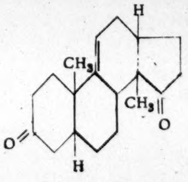
The orientation of substitutents is indicated in the accepted way, the position of the substituent being given and its spatial orientation being indicated by means of the letters α and β (α for trans and β for cis. configuration).



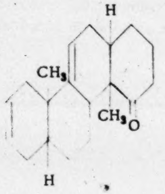
(XXVII)
10,14-Dimethylcardosterane



(XXVIII)
10,14-Dimethyl-8-cardosteren-15-one

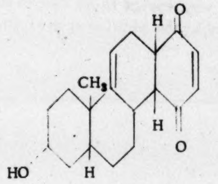


(XXIX)
10,14-Dimethyl-9-cardosterene-3,15-dione



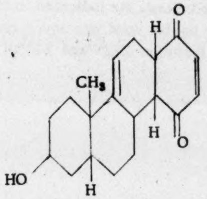
(XXX)

10,14-Dimethyl-2,9-cardo-chrysadien-15-one


H
O
CH$_3$
H
O
HO
H

(XXXI)

10-Methyl-9,16-cardochrysadien-3α-ol-15,17a-dione

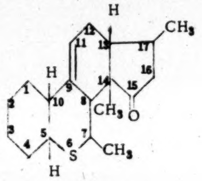

O
H
CH$_3$
H
O
HO
H

(XXXII)

10-Methyl-9,16-cardochrysadien-3β-ol-15,17a-dione

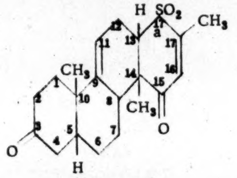
Indication of Hetero Atoms

In the process of complete synthesis compounds may be prepared containing hetero atoms (oxygen, sulfur, or nitrogen) in the steroid nucleus; the following terms are used to indicate these: O – oxa; S – thia; SO_2 – sulfa; NH – aza. The hetero atoms are included in the numbering of the steroid skeleton.


H
CH$_3$
12
11
13
17
16
H
1
9
14
15
2
10
8
CH$_3$
O
3
5
7
4
6
S
CH$_3$
H

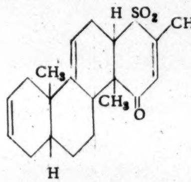
(XXXIII)

7,14,17-Trimethyl-6-thia-9(11)-cardosteren-15-one


H
SO$_2$
CH$_3$
12
17
11
13
a
17
CH$_3$
16
1
9
14
15
2
10
8
CH$_3$
3
5
7
O
4
6
O
H

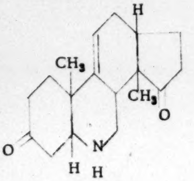
(XXXIV)

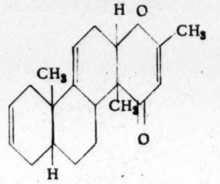
10,14,17-Trimethyl-17a-sulfa-9,16-cardochrysadiene-3,15-dione


H
SO$_2$
CH$_3$
CH$_3$
CH$_3$
O
H

(XXXV)

10,14,17-Trimethyl-17a-sulfa-2,9,16-cardochrysatrien-15-one


H
CH$_3$
CH$_3$
O
O
N
H
H


H
O
CH$_3$
CH$_3$
CH$_3$
O
H

(XXXVI)

10,14-Dimethyl-6-aza-9-cardosterene-3,15-dione

(XXXVII)

10,14,17-Trimethyl-17a-oxa-2,9,16-cardochrysatrien-15-one

We shall use the nomenclature described above in all cases in which the steroid compounds obtained cannot be identified with any natural products.

SUMMARY

A system of nomenclature has been proposed for synthetic steroid compounds.

LITERATURE CITED

[1] Helv. Chim. Acta 34, 1680 (1951).

Received October 7, 1952.

Institute of Organic Chemistry,
USSR Academy of Sciences

ACETYLENE DERIVATIVES

COMMUNICATION 151. HETEROCYCLIC COMPOUNDS

XXVII. SYNTHESIS OF POLYCYCLIC γ-AMINO ALCOHOLS AND THEIR ESTERS*

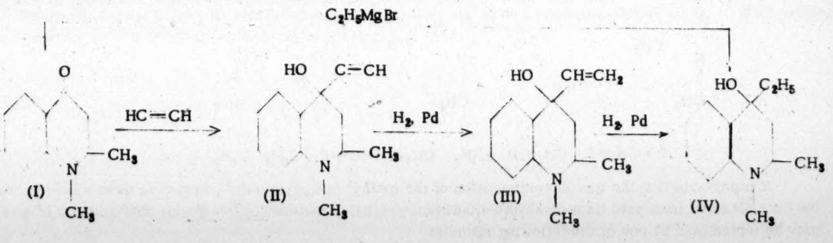
I. N. Nazarov, L. I. Ukhova, and V. A. Rudenko

In the preceding paper [1] we described the synthesis of a number of bicyclic and tricyclic compounds taining a condensed 4-piperidone ring. In view of the fact that certain esters of 4-piperidinols are of high physiological activity, we decided to synthesize a number of bicyclic and tricyclic γ-amino alcohols and their esters.

When octahydro-1,2-dimethyl-4(1H)-quinolone (I) was condensed with acetylene in dry ethereal solution in presence of caustic potash in powder form, 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) was obtained in about 40% yield Numerous attempts to increase the yield by changing the temperature and duration of the reaction did not lead to improved results; an appreciable amount of unchanged ketone (I) was always recovered after the reaction. This ketone condensed with acetylene also in the presence of the potassium derivative of 2-methyl-2-hexanol, but in this case also a considerable proportion of the original ketone (I) was recovered unchanged, and the yield of the acetylenic alcohol (II) was again not more than 40%. The difficulty with which these reactions went was unexpected since we have previously shown in our laboratory [2] that the condensations of various 4-piperidones (including octahydro-2-methyl-4(1H)-quinolone) with acetylene in presence of caustic potash proceed smoothly and give high yields of the corresponding acetylenic alcohols. Finally, we condensed octahydro-1,2-dimethyl-4(1H)-quinolone (I) with sodium acetylide in liquid ammonia [3], and so obtained 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in 82% yield.

It should be noted that the main product of the condensation of acetylene with the ketone (I) was in all cases the crystalline acetylenic alcohol (II), m.p. 130-131°, which on partial hydrogenation (one molecule of hydrogen) in presence of a Pd catalyst gave decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III), m.p. 94-95°, and on exhaustive hydrogenation (two molecules of hydrogen) gave 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°.

In the exhaustive hydrogenation of the acetylenic alcohol (II), prepared in liquid ammonia, a very small amount of a second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) of m.p. 106-106.5° was obtained, and this was the sole product obtained from the reaction of ethylmagnesium bromide on octahydro-1,2-dimethyl-4(1H)-quinolone (I). Thus, exhaustive hydrogenation of the acetylenic alcohol (II) yields the high isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) (m.p. 147-148°), whereas the action of ethylmagnesium bromide on the ketone (I) yields the low melting isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) (m.p. 106-106.5°). A similar phenomenon — a difference in steric directivity in acetylenic and Grignard syntheses — has been observed previously in other cases by Nazarov and Raigorodskaya [2].

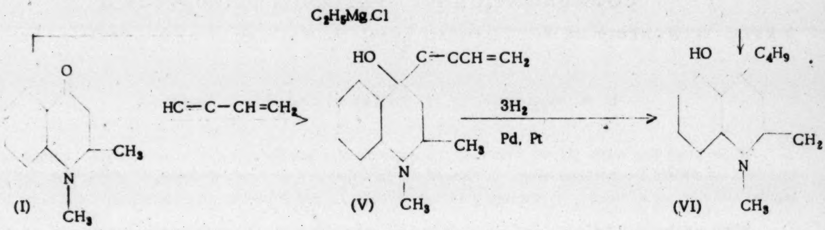


Condensation of octahydro-1,2-dimethyl-4(1H)-quinolone (I) with 1-buten-3-yne in presence of caustic potash powder yielded 4-(3-buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V) in 80% yield, and this, on being fully hydrogenated in presence of Pd and Pt catalysts, yielded 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI), m.p. 119-120°.

---

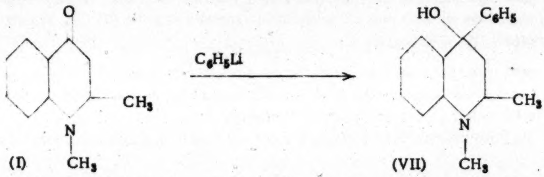
* This article is printed at greater than the prescribed length with the permission of the Editorial Board.

By reaction of octahydro-1,2-dimethyl-4(1H)-quinolone (I) with butylmagnesium chloride, a second isomer of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI) of m.p. 98-99° was obtained. In this case also, therefore, the condensations of 1-buten-3-yne and of butylmagnesium chloride with the ketone (I) differ in steric selectivity:

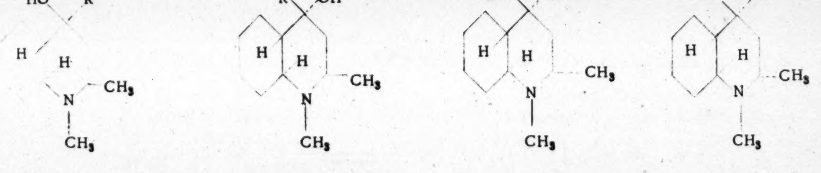

C₄H₉Mg.Cl
O
CH₃
N
(I)
CH₃
HC≡C−CH=CH₂
HO
C≡CCH=CH₂
CH₃
N
(V)
CH₃
3H₂
Pd, Pt
HO
C₄H₉
CH₃
N
(VI)
CH₃

We synthesized also certain tertiary alcohols by the action of phenyllithium on bicyclic and tricyclic compounds containing a condensed 4-piperidone ring.

Reaction of phenyllithium with octahydro-1,2-dimethyl-4(1H)-quinolone (I) gave a 70% yield of a mixture of two crystalline isomers of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII), from which a low melting isomer, m.p. 113-114°, and a high melting isomer, m.p. 167.5-168°, were isolated:

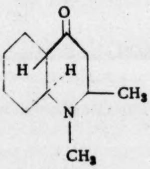

O
CH₃
N
(I)
CH₃
C₆H₅Li
HO
C₆H₅
CH₃
N
(VII)
CH₃

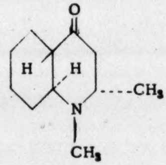
All the above described isomeric alcohols (II−VII) must belong to the trans-decahydroquinoline series, and the difference in their properties must depend solely on the spatial arrangement of the substituents R and OH at $C_{(4)}$ of the decahydroquinoline nucleus:


HO
R
H
H
CH₃
N
CH₃
R
OH
H
H
CH₃
N
CH₃
HO
R
H
H
CH₃
N
CH₃
R
OH
H
H
CH₃
N
CH₃

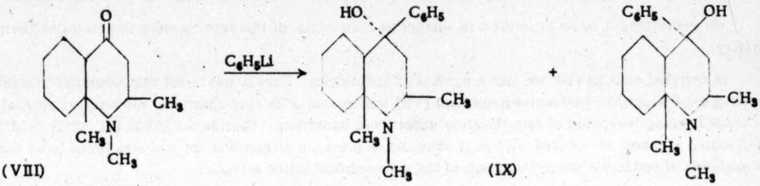
$R = CH{\equiv}C$, $CH_2{=}CH$, C_2H_5, $CH_2{=}CH{-}C{\equiv}C$, C_4H_9, C_6H_5.

It is probable that the spatial configuration of the methyl at $C_{(2)}$ remains constant in these alcohols, for they are obtained from pure trans-octahydro-1,2-dimethyl-4(1H)-quinolone (I), the spatial configuration of which may be represented by one of the following formulas:

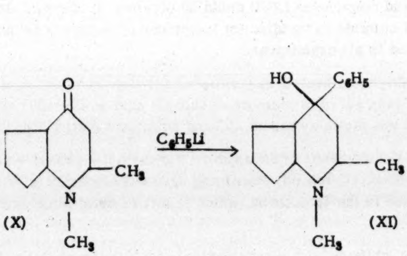

O
H
H
CH₃
N
CH₃


O
H
H
CH₃
N
CH₃

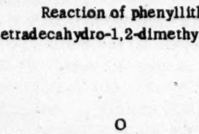
Reaction of phenyllithium with octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII) yielded decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in 62% yield, and this also was isolated in two stereoisomeric forms, m.p. 130-132° and 164-165°:


O
CH₃
N
CH₃
CH₃
(VIII)
C₆H₅Li
HO
C₆H₅
CH₃
N
CH₃
CH₃
(IX)
+
C₆H₅
OH
CH₃
N
CH₃
CH₃

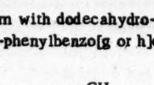
When phenyllithium was condensed with hexahydro-1,2-dimethyl-1,5H-pyrindin-4(1H)-one (X), octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI) was obtained in 66% yield; it was a viscous liquid, and it was not found possible to bring about crystallization:


O
CH₃
N
CH₃
(X)
C₆H₅Li
HO
C₆H₅
CH₃
N
CH₃
(XI)

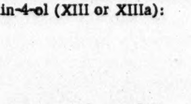
Reaction of phenyllithium with dodecahydro-1,2-dimethylbenzo[g or h]quinolin-4(1H)-one (XII or XIIa) yielded tetradecahydro-1,2-dimethyl-4-phenylbenzo[g or h]quinolin-4-ol (XIII or XIIIa):



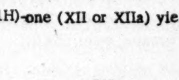
(XII)



(XIIa)

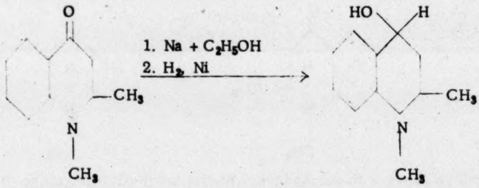

HO
C₆H₅
CH₃
N
CH₃

(XIII)


CH₃
CH₃—N
OH
C₆H₅

(XIIIa)

When octahydro-1,2-dimethyl-4(1H)-quinolone was reduced with sodium in alcohol, or by catalytic hydrogenation, a mixture of stereoisomers of decahydro-1,2-dimethyl-4-quinolinol (XIV) was obtained:



A number of ketones and esters of the piperidine series with strong sedative properties have been recently described in the literature. They include ethyl 1-methyl-4-phenylisonipecotate (Lydol, Dolantin, Demerol) [4], the propionic esters of 1-methyl-4-phenyl-4-piperidinol [5] and 1,3-dimethyl-4-phenyl-4-piperidinol [6], 4-(m-hydroxyphenyl)-1-methyl-4-propionylpiperidine (Cliradon) [7], and others. Among numerous esters of 4-piperidinols synthesized in our laboratory in recent years [8], some were found to have very powerful sedative (analgetic or anesthetic) properties. However, no esters of polycyclic compounds having a condensed piperidine ring have yet been described.

We considered it to be of interest to synthesize compounds of this type in order to determine their physiological activity.

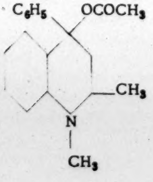
In carrying out this task we met a number of difficulties. Thus it was found that when the lithium derivative of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) was treated with acid chlorides, the original alcohol was recovered unchanged, being incapable of esterification under these conditions. Spassow's method [9], which readily yields esters when amino alcohols are treated with acid chlorides in presence of magnesium, was also found to be inapplicable to the synthesis of tertiary α-phenyl alcohols of the decahydroquinoline series.

When the alcohol (VII) was treated with acetic or propionic anhydride in presence of sulfuric acid, the original alcohol was again recovered unchanged, no esterification occurring. Esters of both of the isomers of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) were obtained by the action of acid anhydrides in pyridine at 140°. However, only the acetates (XV) and propionates (XVI) could be obtained in this way, and all attempts to prepare the benzoates by the action of benzoyl chloride in pyridine (or in absence of pyridine) did not give positive results, unchanged alchol (VII) being recovered in all experiments.

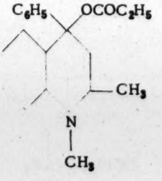
When acetic anhydride was heated with either of the isomers of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in pyridine at 140-180° or in presence of sulfuric acid at 100-120°, the original tertiary alcohol (IX) was recovered unchanged, as was shown by mixed melting point tests on the hydrochlorides.

This difference in the behaviors of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) and decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) toward esterifying agents is evidently to be explained by the presence in the latter of an angular methyl group in the 8a-position, which results in steric hindrance to the esterification of the hydroxyl in the 4-position.

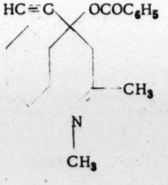
Reaction of benzoyl chloride with 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in pyridine at 100° yielded its benzoic ester (XVII), and reaction of benzoyl chloride with decahydro-1,2-dimethyl-4-quinolinol (XIV) yielded its benzoic ester (XVIII):



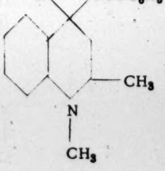
(XV)



(XVI)



(XVII)



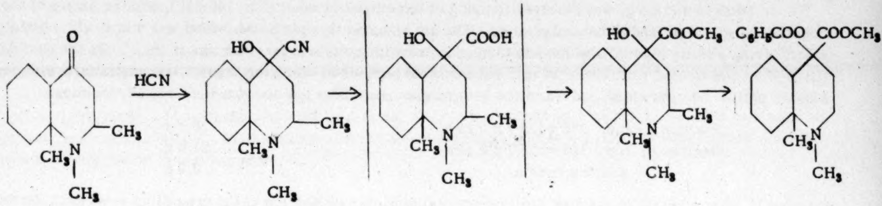
(XVIII)

The benzoic esters (XVII and XVIII) did not give stable crystalline salts, and were therefore not tested.

Physiological tests on the acetate (XV) and the propionate (XVI) (high melting isomers) showed that both of these compounds had anesthetic action, which was more marked in the propionic ester. The activities of these compounds, however, were lower than those of preparations now in use in medical practice, and their toxicities were higher.

The cyanohydrin (XIX) was obtained from octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII), and this, on being hydrolyzed, gave the corresponding hydroxy acid (XX), which was obtained in the form of its hydrochloride.

Esterification of this acid with methanol, with passage of hydrogen chloride, yielded methyl decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI), m.p. 138-139°, and by the action of benzoyl chloride on this hydroxy ester, methyl 4-benzoyloxydecahydro-1,2,8a-trimethylcinchoninate (XXII), m.p. 256-257°, was obtained:



(VIII) (XIX) (XX) (XXI) (XXII)

The benzoic ester (XXII) is close in structure to α-eucaine; physiological tests on this substance will therefore be of interest.

EXPERIMENTAL

4-Ethynyldecahydro-1,2-dimethyl-4-quinolinol (II)

a) Liquid ammonia (300 ml) was placed in a three-necked, round-bottomed flask fitted with mechanical stirrer, reflux condenser, dropping funnel, thermometer, and tube for passage of acetylene. The flask was cooled with a mixture of dry ice and methanol (−70°), and sodium (9 g) was added in small pieces. When the whole of the sodium had dissolved, passage of acetylene was begun and about 60 liters passed into the flask in the course of three hours. Then, with continuous stirring and passage of acetylene, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (30 g), b.p. 100-102°/2 mm, n_D^{19} 1.4980 [10], in an equal volume of dry ether was added dropwise over a period of 20 minutes. After addition of the ketone, acetylene was passed for a further 90 minutes, and the reaction mixture was set aside overnight. On the next day ammonium chloride (30 g) and water (50 ml) were added to the reaction mixture at −15°. The mixture was repeatedly extracted with ether, and the ethereal solution was neutralized with carbon dioxide until it became clear; it was then dried with magnesium sulfate and vacuum-fractionated, yielding 28.3 g (82%) of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) as a colorless, very viscous (glasslike) liquid, b.p. 129-131°/3 mm.

Found %:	C 75.09; 74.93;	H 10.51; 10.50
$C_{13}H_{21}ON$. Calculated %:	C 75.29;	H 10.21

This substance is of good solubility in alcohol, benzene, chloroform, carbon tetrachloride, dioxane, acetone, and various gasoline fractions.

b) A mixture of 18.6 g of caustic potash in powder form and 200 ml of dry ether was saturated with acetylene, which was passed for one hour at −3°. A solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (30 g) in dry ether (30 ml) was then added dropwise for a period of one hour with continuous stirring and passage of acetylene, which was then passed for a further period of 4 hr, 30 min., the temperature being maintained at −3° throughout. On the next day the reaction mixture was treated with 30 ml of water, and the product was carefully extracted with ether; the ether extract was neutralized with carbon dioxide until it became clear, and was then dried with magnesium sulfate and vacuum-fractionated, yielding 27.3 g of a colorless viscous liquid, b.p. 134-137°/4 mm, which, on being diluted with gasoline (b.p. 80-100°), partially crystallized out. Two recrystallizations from gasoline yielded 4 g of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in the form of colorless crystals, m.p. 130-131°;

Found %: N 6.77; 6.79
$C_{13}H_{21}ON$. Calculated %: N 6.75

The picrate, recrystallized from alcohol, melted at 188-189°.

The noncrystallizing mother liquor, after separation of the crystals of the acetylenic alcohol (II), was vacuum-distilled, yielding a fraction (I, 8g), b.p. 130-137°/5 mm, which appeared to be a mixture of the original ketone (I) and the acetylenic alcohol (II), and a fraction (II, 9 g), b.p. 137-139° 5mm), which appeared to be the pure acetylenic alcohol (II). The total yield of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol was 13 g [about 40% on the amount of the ketone (I) taken].

c) Potassium (19.5 g) was dissolved in 232 g of 2-methyl-2-hexanol (b.p. 140-141°), and the excess of the alcohol was distilled off under reduced pressure. The dry alkoxide that remained behind was mixed with absolute ether, giving a slurry (150 ml), which was then saturated with acetylene for two hours at −10°. On the next day the product was treated with water (30 ml) and extracted with ether; the ether extract was neutralized with carbon dioxide until it became clear, and was dried with magnesium sulfate and vacuum-fractionated, yielding:

Fraction I,	b.p. 103−125°/2.5 mm	5.1 g
Fraction II,	b.p. 125−128°/2.5 mm	21.5 g
	Resinous residue	3.0 g

Fraction II, after addition of gasoline and three crystallizations, yielded 6 g of the crystalline acetylenic alcohol (II), m.p. 130-131°. The noncrystallizing mother liquor was vacuum-distilled, yielding 3 g of a mixture of the original ketone (I) and the acetylenic alcohol (II), b.p. 120-130°/3 mm, and 8 g of a viscous liquid, b.p. 130-132°/3 mm, which solidifed to a glasslike mass and appeared to be pure acetylenic alcohol (II). The total yield of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol was 14 g [about 41% on the amount of ketone (I) taken]

Decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III)

The crystalline acetylenic alcohol (II) (3 g; m.p. 130-131°) was dissolved in ethanol (20 ml) and hydrogenated in the presence of a Pd catalyst When 351 ml (19°, 748.6 mm) of hydrogen had been absorbed, the process was discontinued The alcohol was distilled off, and the residue was vacuum-distilled, yielding 2.5 g of decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III), b.p. 132-134°/ 5 mm, which rapidly crystallized out. After three crystallizations from petroleum ether it melted at 93.5-95°.

Found %: C 74.77; 74 71; H 11.00; 10.99
$C_{13}H_{23}ON$. Calculated %: C 74.92; H 11.07

4-Ethyldecahydro-1,2-dimethyl-4-quinolinol (IV)

a) The crystalline alcohol (II) (m.p. 130-131 °; 0.9 g) was dissolved in ethanol (10 ml) and hydrogenated in presence of a Pd catalyst. When 200 ml (19°, 744.7 mm) of hydrogen had been absorbed, the process was discontinued (theoretically, 217 ml of hydrogen is required for the complete hydrogenation of the triple bond). The catalyst was filtered off, the alcohol was distilled off, and the crystals that came down were recrystallized twice from gasoline, yielding 0.7 g of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°.

Found %: C 73.73; 73.93; H 12.01; 11.83
$C_{13}H_{25}ON$. Calculated %: C 73.87 H 11.92

A similar result was obtained also when the above described (b) liquid fraction of the acetylenic alcohol (II), b.p. 137-139°/5 mm, was exhaustively hydrogenated. The isomer of the saturated alcohol (IV) obtained by this method did not give a picrate.

b) Magnesium turnings (4.5 g) and absolute ether (100 ml) were introduced into a three-necked, round-bottomed flask, and ethyl bromide (20 g) was added dropwise. To the ethylmagnesium bromide so obtained, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (16.5 g) in an equal volume of absolute ether was added dropwise, with stirring and cooling with ice water. The reaction mixture was stirred for one hour at room temperature and then set aside overnight. On the next day it was boiled for two hours. After removal of ether and addition of 70 ml of absolute toluene, the mixture was stirred for a further 2 hr, 30 min at the temperature of boiling toluene. The reaction mixture was then treated with 15% hydrochloric acid (25 ml) and the toluene layer was separated and extracted with 15% hydrochloric acid (20 ml). The united aqueous layer was saturated with solid caustic alkali, and the base that separated was extracted with ether. The ether layer was dried with magnesium sulfate and vacuum-fractionated, yielding 9 g of the original ketone (I); b.p. 108-110°/5 mm; n_D^{20} 1.4950) and 3.4 g of a colorless liquid, b.p. 129-131°/5 mm, which crystallized out in the receiver. After two recrystallizations from gasoline, 2.9 g of the second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 106-106.5°, was obtained.

Found %: C 74.00; 74.10; H 12.14; 11.91
$C_{13}H_{25}ON$. Calculated %: C 73.87 H 11.92

Found %: OH 7.71 (by Chugaev-Tserevitinov method)
$C_{13}H_{24}(OH)N$. Calculated %: OH 8.04

The picrate, after recrystallization from alcohol, melted at 164.5-166°.

c) The acetylenic alcohol formed by the condensation reaction in liquid ammonia (II), b.p. 129-131°/3 mm; (see a) in the section relating to this substance) (6 g) was dissolved in ethanol (60 ml) and hydrogenated in the presence of a Pd catalyst, 1420 ml (20°, 745 mm) of hydrogen being absorbed. The catalyst was filtered off, the alcohol was distilled off, and the product was vacuum-distilled, yielding 4.7 g of a colorless liquid, b.p. 115-116°/2 mm, which crystallized out in the receiver. After recrystallization from gasoline, the product melted at 90-140°. Fractional crystallization yielded 3.9 g of the above described isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°. From the mother liquor, after long standing, a few crystals of the second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol appeared, and these, after being washed with gasoline and dried in a vacuum desiccator, melted at 104-105°. In admixture with the above described sample obtained by the Grignard method, it showed no depression in melting point.

4-(3-Buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V)

Caustic potash in powder form (14 g) and dry ether (50 ml) were introduced into a round-bottomed flask, and in small portions, with continuous stirring and cooling to −10°, 1-buten-3-yne (30 g) and octahydro-1,2-dimethyl-4(1H)-quinolone (I) (25 g) dissolved in dry ether (30 ml) were added. The reaction mixture was cooled with ice water and stirred for 6 hrs. 30 min.; on the next day it was treated with water (20 ml). The product was extracted with ether, and the ether extract was neutralized with carbon dioxide until clear, dried with magnesium sulfate, and vacuum distilled in a current of nitrogen, yielding 25 g of 4-(3-buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V) in the form of a clear colorless liquid, b.p. 138-140°/2mm, which solidified after the distillation to a glasslike mass.

Found %: N 5.79; 5.73
$C_{15}H_{23}ON$. Calculated %: N 6.00

4-Butyldecahydro-1,2-dimethyl-4-quinolinol (VI)

a) The freshly distilled α-butenynyl alcohol (V) (b.p. 138-140°/2 mm; 3.3 g) was dissolved in ethanol (20 ml) and hydrogenated in presence of a Pd catalyst, the process being discontinued when 700 ml of hydrogen had been absorbed. A portion of Pt catalyst was added, and a further 325 ml of hydrogen was absorbed. The theoretically required amount of hydrogen was 1054 ml (16°, 746 mm). The catalyst was filtered off, the alcohol was distilled off, and the product was vacuum-distilled, yielding 2.6 g of a colorless, not particularly viscous liquid, b.p. 115-117°/2.5 mm, which partially crystallized out in a short time. Two crystallizations from gasoline yielded 1.05 g of crystals of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI), m.p. 119-120°, readily soluble in alcohol, benzene, chloroform, carbon tetrachloride and acetone.

Found %: C 75.61; 75.42; H 12.32; 12.22
$C_{15}H_{29}ON$. Calculated %: C 75.25; H 12.21

b) Magnesium turnings (4 g), absolute ether (50 ml), and butyl chloride (15.3 g) were introduced into a round-bottomed flask, and to the Grignard reagent so prepared, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (15 g) in absolute ether (15 ml) was added with stirring and cooling (ice water). Stirring was continued for five hours with cooling and for five hours at the boiling point of ether. The reaction mixture was cooled, and 15% hydrochloric acid (120 ml) was added. The ether layer was separated and extracted with dilute hydrochloric acid, and the united aqueous layer was saturated with solid caustic alkali. The product was carefully extracted with ether, and the extract was neutralized with carbon dioxide, dried with magnesium sulfate, and vacuum-fractionated, yielding 7.4 g of a colorless viscous liquid, b.p. 124-128°/5 mm, which slowly crystallized out. Crystallization was appreciably accelerated by addition of ligroin. After six crystallizations, 2.9 g of the second isomer of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI) was obtained in the form of colorless needles, m.p. 98-99°.

Found %: C 75.55, 75.45; H 12.25, 12.25
$C_{15}H_{29}ON$. Calculated %: C 75.25; H 12.21
Found %: OH 7.29 (by Chugaev-Tserevitinov method)
$C_{15}H_{28}(OH)N$. Calculated %: OH 7.11.

Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII)

All syntheses with organolithium compounds were carried out in a current of dry nitrogen. Absolute ether (250 ml) and finely cut lithium (7.2 g) were introduced into a round-bottomed flask fitted with mechanical stirrer, reflux condenser, dropping funnel, thermometer, and tube for passage of nitrogen, and a solution of bromobenzene (78 g) in absolute ether (75 ml) was added dropwise. When reaction had ceased, the mixture was heated at the boiling point of ether for two hours. To the phenyllithium so prepared, a solution of 60 g of octahydro-1,2-dimethyl-4(1H)-quinolone (b.p. 108-110°/4 mm, n_D^{20} 1.4975) in 75 ml of absolute ether was added dropwise with continuous stirring at −12° over a period of five hours. The reaction mixture was stirred with cooling for 40 minutes, and was then set aside overnight. On the next day it was stirred again for three hours at the temperature of boiling ether, and was then treated with 100 ml of water. The ether layer was separated, and the aqueous layer was saturated with caustic alkali and extracted with ether. The united ether solution was dried with magnesium sulfate, and the ether was driven off, when the residue partially crystallized out. It was filtered at the pump, yielding 40.7 g of crystals, m.p. 105-159°, from which, by fractional crystallization from acetone, 9.7 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) was isolated in the form of well-defined needles, m.p. 167.5-168°.

Found %: C 78.36, 78.51; H 9.86, 9.69
$C_{17}H_{25}ON$. Calculated %: C 78.71; H 9.71.

The hydrochloride of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol melted at 279-280° (from a mixture of alcohol and ether). Its picrate melted at 220-221° (from alcohol). In addition to the 9.7 g of high-melting isomer, the 40.7 g of crystals yielded also 25 g of a crystalline mixture of the isomers, m.p. 128-145°.

The mother liquor remaining after separation of the main crop (40.7 g) of crystals was evaporated down and set aside at room temperature. After three days crystallization had occurred. After three recrystallization from ligroin, 13.5 g of the low-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol was isolated in the form of a finely crystalline powder, m.p. 113-114°.

Found %: C 78.76, 79.02; H 9.81, 9.78
$C_{17}H_{25}ON$. Calculated %: C 78.71; H 9.71.

The picrate of the low-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol melted at 191-192° (from alcohol).

In this experiment, therefore, 9.7 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (m.p. 167.5-168°), 13.5 g of the low-melting isomer (m.p. 113-114°), and 25 g of a crystalline mixture of the two isomers (m.p. 128-145°) were isolated.

Decahydro-1,2,8a-trimethyl-4-phenyl-4-phenyl-4-quinolinol (IX)

A solution of 60 g of octahydro-1,2,8a-trimethyl-4 (1H)-quinolone (VIII) (b.p. 103-104°/3 mm; n_D^{20} 1.5018) in an equal volume of absolute ether was added dropwise with continuous stirring at −10° to phenyllithium prepared from 6.5 g of lithium and 72.3 g of bromobenzene dissolved in 300 ml of absolute ether. After the ketone had been added, stirring was continued with cooling (−5-10°) for one hour, then at room temperature for one hour, and finally on the next day at the temperature of boiling ether for four hours Water (100 ml) was added, the ether layer was separated, and the aqueous layer was saturated with caustic alkali and extracted with ether. The united ether solution was dried with sodium sulfate, the ether was driven off, and the residue was vacuum-distilled, yielding 52.6 g of a viscous liquid, b.p. 155-159°/0.02 mm, which quickly crystallized out. Fractional crystallization from acetone yielded 12.4 g of the high-melting isomer of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in the form of large needles, m.p. 164-165°.

Found %: C 79.23, 79.00; H 9.98, 10.03
$C_{18}O_{27}ON$. Calculated %: C 79.07; H 9.95.

The hydrochloride melted at 255-256° (from alcohol).

In addition 3.7 g of the low-melting isomer of decahydro-1,28a-trimethyl-4-phenyl-4-quinolinol was isolated in the form of small prisms, m.p. 130-132°.

Found %: C 79.30, 79.62, 79.21; H 9.74, 9.94, 10.13
$C_{18}H_{27}ON$. Calculated %: C 79.07; H 9.95.

The hydrochloride melted at 284-285° (from alcohol).

The remaining portion of substance obtained (30.3 g) was a mixture of the two isomers of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol, m.p. 138-150°.

Octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI)

A solution of 9.5 g of hexahydro-1,2-dimethyl-1,5H-pyrindin-4(1H)-one (X) (b.p. 85-87°/ 2 mm; n_D^{20} 1.4915) in 10 ml of absolute ether was added dropwise with stirring at −12° over a period of one hour to phenyllithium prepared from 1.2 g of lithium and 13.3 g of bromobenzene in 100 ml of absolute ether. The reaction mixture was stirred for one hour with cooling, for one hour at room temperature, and for three hours on the next day at the boiling point of ether. The product was hydrolyzed with water (20 ml), the ether layer was separated, and the aqueous layer was saturated with solid caustic alkali and extracted with ether The united ether solution was dried with sodium sulfate, the ether was driven off, and the residue was vacuum-fractionated, yielding 9.2 g of octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI) in the form of a viscous liquid, b.p. 147-151°/ 0.07 mm; n_D^{20} 1.5474; d_4^{20} 1.0613; Found MR 73.24; Calculated MR 73.55.

Found %: C 78.56, 78.42; H 9.38, 9.46
$C_{16}H_{23}ON$. Calculated %: C 78.32; H 9.44.

Tetradecahydro-1,2-dimethyl-4-phenylbenzo [g or h] quinolin-4-ol (XIII or XIIIa)

A solution of 9 g of dodecahydro-1,2-dimethylbenzo[g or h] quinolin-4-(1H)-one (XII or XIIa) (b.p. 142-143°/3 mm; n_D^{20} 1.5210) in 15 ml of absolute ether was added dropwise with stirring at − 12° to phenyllithium prepared in a round-bottomed flask from 1.35 g of lithium and 15 g of bromobenzene in 100 ml of absolute ether. The reaction mixture was stirred for one hour with cooling and for three hours on the next day at the boiling point of ether; it was then cooled, and decomposition was effected by addition of 20 ml of water. The ether layer was separated, and the aqueous layer was saturated with solid caustic alkali and extracted with ether. The united ether solution was dried with sodium sulfate, ether was distilled off, and the residue was vacuum-fractionated, yielding 9.7 g of tetrahydro-1,2-dimethyl-4-phenylbenzo[g or h]quinolin-4-ol (XIII or XIIIa), b.p. 167-172°/ 0.02 mm, which solidified to a glass-like mass in the receiver.

Found %: C 80.34, 80.39; H 10.08, 9.89
$C_{22}H_{31}ON$. Calculated %: C 80.45; H 9.96.

Decahydro-1,2-dimethyl-4-quinolinol (XIV)

a) A solution of 24 g of octahydro-1,2-dimethyl-4 (1H)-quinolone (b.p. 107-108°/4 mm; n_D^{20} 1.4980) in 470 ml of alcohol was placed in a round-bottomed flask. The solution was stirred continuously, and sodium (42 g) was added in small pieces over a period of 90 minutes, after which the reaction mixture was stirred further for two hours The solution was acidified with 20% hydrochloric acid (300 ml), and the precipitate of sodium chloride that formed was filtered off and washed with hot alcohol. The filtrate was evaporated down under reduced pressure to 150-200 ml, and the base was liberated by addition of solid caustic alkali and extracted with ether. The ether solution was dried with potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled, yielding 15.4 g of decahydro-1,2-dimethyl-4-quinolinol in the form of a colorless viscous liquid having a feeble amine odor, b.p. 114-115.5° at 2 mm.

Found %: C 71.82, 72.07; H 11.74, 11.50
$C_{11}H_{21}ON$. Calculated %: C 72.07; H 11.54
Found %: OH 9.18 (by Chugaev-Tserevitinov method)
$C_{11}H_{20}(OH)N$. Calculated %: OH 9.27

b) A solution of 7.9 g of octahydro-1,2-dimethyl-4(1H)-quinolone (b.p. 107-108°/ 3 mm; n_D^{20} 1.4980) in 50 ml of alcohol was placed in an autoclave, and 0.3 g of a nickel catalyst was added. The substance was hydrogenated under 90 atm at 150° for 30 minutes. The catalyst was filtered off, the alcohol was distilled off, and the residue was vacuum-distilled, yielding 5.7 g of decahydro-1,2-dimethyl-4-quinolinol (XIV) in the form of a colorless viscous liquid, b.p. 124-125.5°/4 mm.

Found %: OH 9.03, 8.96 (by Chugaev-Tserevitinov method)
$C_{11}H_{20}(OH)N$. Calculated %: OH 9.27

Acetic Ester of the High-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XV)

A solution containing 5 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) (m.p. 167.5-168°), 20 ml of acetic anhydride, and 20 ml of pyridine was heated under reflux for eight hours at 140°. The pyridine and excess of acetic anhydride were driven off under the vacuum from a water pump, and to the residue a saturated solution of potassium carbonate was added to alkaline reaction (20 ml). The product was extracted with ether, and the ether extract was dried with magnesium sulfate. The residue after removal of ether crystallized out completely. After being boiled with active charcoal in benzene and then recrystallized from ligroin, the acetic ester of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol obtained in this way melted at 122-123°.

Found %: C 75.85, 76.07; H 9.19, 9.17
$C_{19}H_{27}O_2N$. Calculated %: C 75.71; H 9.02.

By the action of dry hydrogen chloride on an ethereal solution of the base, the hydrochloride of the acetic ester of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol was obtained. After recrystallization from acetone it melted at 241-242°.

Acetic Ester of the Low-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XV)

A solution containing 1 g of the α-phenyl alcohol (m.p. 112-114°), 3 ml of acetic anhydride, and 3 ml of pyridine was heated at 140° for five hours. The pyridine and acetic anhydride were driven off, and the residue was diluted with 7 ml of water, saturated with potassium carbonate, and extracted with ether. The ether extract was dried with magnesium sulfate, and the liquid residue remaining after removal of ether was converted into its hydrochloride. The hydrochloride, which was obtained in the first place as an oil, was converted into a powder when rubbed out under absolute ether. After being reprecipitated twice from absolute alcohol by absolute ether, the hydrochloride was obtained in the form of crystals (0.3 g), m.p. 225-225.5°.

Found %: C 66.20, 66.31; H 8.57, 8.46; Cl 10.16, 10.57
$C_{19}H_{28}O_2NCl$. Calculated %: C 67.53; H 8.36; Cl 10.49.

Propionic Ester of the High-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XVI)

a) A solution containing 10 g of the α-phenyl alcohol VII of m.p. 167.5-168°, 35 ml of propionic anhydride, and 35 ml of pyridine was heated under reflux at 140-150° for eight hours The pyridine and excess of anhydride were driven off, and to the residue 30 ml of saturated potassium carbonate solution and then dry potassium carbonate were added The product was extracted with ether, and the ether extract was dried with magnesium sulfate. The product after removal of ether was converted into its hydrochloride (10.5 g of crude hydrochloride). Two reprecipitations from a mixture of absolute alcohol and ether yielded 7.5 g of the propionic ester of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol hydrochloride, m.p. 230-231°.

Found %: C 68.35, 68.44; H 8.63, 8.60; Cl 9.95, 9.92
$C_{20}H_{30}O_2NCl$. Calculated %: C 68.22; H 8.59; Cl 10.08.

b) A drop of sulfuric acid was added to a solution of 1.4 g of the α-phenyl alcohol VII of m.p. 165-166.5° in 15 ml of propionic anhydride, and the mixture was heated for four hours at 100°. The propionic anhydride (excess) was driven off, and the residue was diluted with 2 ml of water and saturated with sodium carbonate. The base was extracted with ether, and the ether extract was dried with magnesium sulfate, distilled to remove ether, and vacuum-distilled, yielding 0.8 g of viscous yellow liquid, b.p. 140°/0.02 mm, which crystallized out when rubbed. Two recrystallizations from ligroin yielded 0.6 g of crystals, m.p. 165-166.5°. In admixture with the original α-phenyl alcohol it showed no depression of melting point.

Propionic Ester of the Low-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XVI)

A solution of 6.8 g of the α-phenyl alcohol (VII) of m.p. 113-115° in 21 ml of propionic anhydride and 16 ml of pyridine was heated at 145-150° for nine hours. The excess of propionic anhydride and pyridine were driven off under the vacuum from a water pump, and the residue was diluted with 20 ml of water and saturated with potassium carbonate until a slurry was formed. The base was carefully extracted with ether, dried with magnesium sulfate, and after distillation, converted into the hydrochloride. The oily hydrochloride so obtained was dissolved in the least possible amount of absolute alcohol, and absolute ether was added to the solution until a turbidity was produced. After prolonged standing, 1.3 g of crystals of the hydrochloride of the propionic ester of the low-melting isomer of decahydro-1,2-dimethyl-4-quinolinol, m.p. 195-196°, was obtained.

Found %: C 68.13, 68.17; H 8.63, 8.54

$C_{20}H_{30}O_2NCl$. Calculated %: C 68.22; H 8.59.

Benzoic Ester of 4-Ethynyldecahydro-1,2-dimethyl-4-quinolinol (XVII)

A solution of 7 g of the acetylenic alcohol II of b.p. 129-131°/3mm in 35 ml of pyridine and 16 ml of benzoyl chloride was heated under reflux in a boiling water bath for four hours. The pyridine and excess of benzoyl chloride were distilled off, and ether was added to the residue; no crystals appeared. The residue was dissolved in 30 ml of water, the base was carefully separated with cooling by means of sodium carbonate, and was then extracted with ether, the extract being neutralized with carbon dioxide and dried with magnesium sulfate. The residue after removal of ether was a dark-colored resin containing crystals. These were extracted and recrystallized from benzene. The product was 0.39 g of the benzoic ester of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol, m.p. 174-175°.

Found %: C 76.87, 76.82; H 8.32, 8.29

$C_{20}H_{25}O_2N$. Calculated %: C 77.07; H 8.09.

The residual mass was a nondistilling resin. It was not found possible to obtain the hydrochloride of the benzoic ester of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol in a crystalline form.

Benzoic Ester of Decahydro-1,2-dimethyl-4-quinolinol (XVIII)

A solution of 4 g of decahydro-1,2-dimethyl-4-quinolinol (XIV) (b.p. 124-125°/4 mm) in 10 ml of benzoyl chloride was saturated with gaseous hydrogen chloride and heated at 100° for five hours. The excess of benzoyl chloride was driven off in a water bath under the vacuum from a water pump. The residue was extracted with ether, and was then diluted with 12 ml of water. Potassium carbonate was added, and the base was extracted with ether. The ether extract was dried with magnesium sulfate, the ether was distilled off, and the residue was distilled, yielding 2.8 g of the benzoic ester of decahydro-1,2-dimethyl-4-quinolinol in the form of a very viscous liquid, b.p. 154-156°/2 mm.

Found %: C 74.83, 74.67; H 8.31, 8.21

$C_{18}H_{25}O_2N$. Calculated %: C 75.22; H 8.75

It was not found possible to isolate the hydrochloride of the benzoic ester of decahydro-1,2-dimethyl-4-quinolinol in a crystalline form.

Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninonitrile (XIX)

a) Hydrochloric acid (12 ml, 1 : 1) was added to 10 g of octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII) (b.p. 103-104°/3 mm; n_D^{20} 1.5020), and with stirring and cooling to 0° a solution of 4 g of potassium cyanide in 6 ml of water was added. The medium became weakly alkaline, and after a few minutes crystals appeared. The reaction mixture was stirred further for two hours at room temperature. The crystals were extracted with ether, and the ether solution was dried with sodium sulfate. The ether was driven off, and the residue, a thick oil, partially crystallized out after a short time, yielding 1.6 g of crystals, m.p. 102-107°. Melting point after recrystallization from acetone 118-120°. The mother liquor was distilled, yielding 4.9 g of the original quinolone, b.p. 102-105°/3 mm, n_D^{23} 1.5000.

Analysis of crystals m.p. 118-120°:

Found %: N 12.60, 12.54

$C_{13}H_{22}ON_2$. Calculated %: N 12.60

b) Hydrochloric acid (16 ml, 1 : 1) was added to 10 g octahydro-1,2,8a-trimethyl-4 (1H)-quinolone (VIII) (b.p. 103-104° at 3 mm; n_D^{20} 1.5020), and with stirring and cooling to 0° 4 g of potassium cyanide was added. Stirring was continued for 90 minutes. The medium was acid in reaction, and a solution of potassium carbonate was added to neutral reaction; dry potassium carbonate was then added. The product was extracted with ether, and the ether extract was dried with sodium sulfate. The ether was driven off, and the residue partially crystallized out, yielding 3.2 g of crystals of the cyanohydrin, m.p. 102-107°. After recrystallization from acetone the substance melted at 118-120°.

Methyl Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI)

Concentrated hydrochloric acid (15 ml) was added to 3 g of the cyanohydrin, and the solution was heated in a boiling water bath for ten hours. The hydrochloric acid was evaporated off in a porcelain dish on a water bath. Absolute alcohol was added to the dry residue, and the precipitate of ammonium chloride was filtered off. The alcohol was driven off, yielding as residue the hydrochloride of decahydro-4-hydroxy-1,2,8a-trimethylcinchoninic acid (XX) in the form of a viscous liquid.

To the hydrochloride of the hydrolysis product (XX), 20 ml of absolute methanol was added, and dry hydrogen chloride was passed through the mixture at the boiling point of the alcohol for two hours. The methanol and hydrogen chloride were removed under reduced pressure, and to the residue, a thick dark-colored liquid, 10 ml of water and some potassium carbonate were added. The base was extracted with ether, and the ether extract was dried with sodium sulfate. The residue after removal of ether was 1.6 g of crystalline methyl decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI), which melted, after two recrystallizations from acetone, at 138-139°.

Found %: C 65.76, 65.56; H 9.93, 9.82
$C_{14}H_{25}O_3N$. Calculated %: C 65.84; H 9.86.

Methyl 4-Benzoyloxydecahydro-1,2,8a-trimethylcinchoninate (XXII)

Benzoyl chloride (5 ml) was added to 1 g of the hydroxy ester XXI. The reaction was carried out for five hours in a boiling water bath, and for one hour at 130-140°. The benzoyl chloride was removed in a boiling water bath under the vacuum from a water pump. Water (10 ml) was added to the viscous dark-colored residue. Residual benzoyl chloride was extracted with ether. The base was liberated with potassium carbonate and extracted with ether. The ether solution was dried with sodium sulfate. The ether was driven off, and the residue crystallized out. The product after recrystallization from acetone, was 0.15 g of substance of m.p. 256-257°.

Found %: C 69.14, 69.15; H 7.95, 8.07
$C_{21}H_{29}O_4N$. Calculated %: C 70.19; H 8.07

SUMMARY

1. Various alcohols of the decahydroquinoline, perhydro-1-pyrindine, and perhydrobenzoquinoline series have been synthesized.

2. Six esters of the decahydroquinoline series have been prepared.

3. Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninonitrile, the corresponding acid, and its esters have been synthesized.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 55. APPLICATION OF INTERCHAIN EXCHANGE REACTIONS IN LINEAR POLYCONDENSATION PROCESSES

S. R. Rafikov, V. V. Korshak, and G. N. Chelnokova

It has been shown in a series of investigations in our laboratory [1] that the linear-polycondensation reaction is a very complex equilibrium process involving both synthetic and degradational reactions. We have shown also, working with polyesters [2] and polyamides [3], that the linear-polycondensation reaction leads to the formation of products having a comparatively low degree of polydispersity, which is contrary to the predictions of the mechanical theories of Flory [4] and Schulz [5]. The main cause of the equalization of chain lengths in the polymer formed is the occurrence of exchange reactions between the growing polymer chains — reactions of interchain exchange, consisting in interaction between chains of different lengths involving not only active end groups, but also the bonds between individual structural units of the macromolecule. These two types of reactions may be represented in a general way by the following equations:

For polyesters —

$$\mathrm{H(ORO-COR'CO)_xOH + H(ORO-COR'CO)_yOH \rightleftharpoons H(ORO-COR'CO)_mOH + H(ORO-COR'CO)_nOH.} \quad \text{(I)}$$

For polyamides —

$$\mathrm{H(NHRNH-COR'CO)_xOH + H(NHRNH-COR'CO)_yOH \rightleftharpoons H(NHRNH-COR'CO)_mOH + H(NHRNH-COR'CO)_nOH.} \quad \text{(Ia)}$$

where $m + n = x + y$.

The processes represented by these equations (I and Ia) proceed for these classes of compounds by acidolysis, alcoholysis, and aminolysis reactions and involve the reaction of an end group of one of the reacting molecules with the ester, amide, or other linkage of another molecule.

However, as we have shown in a number of cases, interchain exchange may proceed also by the mechanism of transesterification, transamidation, or the like, i.e. by reaction between ester, amide, or other linkages of one molecule with similar linkages in another molecule, as shown in Equations II and IIa:.

$$\begin{gathered}\mathrm{H(ORO-COR'CO)_x \,\vdots\, (OROCOR'CO)_yOH + HO(COR'CO-ORO)_m \,\vdots\, (COR'CO-ORO)_nH} \rightleftharpoons \\ \rightleftharpoons \mathrm{H(ORO-COR'CO)_x-(OROCOR'CO)_mOH + HO(COR'CO-ORO)_y-(COR'CO-ORO)_nH,}\end{gathered} \quad \text{(II)}$$

where $x + y \neq x + m$.

$$\begin{gathered}\mathrm{H(NHRNH-COR'CO)_x \,\vdots\, (NHRNH-COR'CO)_yOH + HO(COR'CO-NHRNH)_m \,\vdots\, (COR'CO-NHRNH)_nH} \rightleftharpoons \\ \rightleftharpoons \mathrm{H(NHRNH-COR'CO)_x-(NHRNH-COR'CO)_mOH + HO(COR'CO-NHRNH)_y-(COR'CO-NHRNH)_nH.}\end{gathered} \quad \text{(IIa)}$$

In a series of previous investigations we have shown that acidolysis, aminolysis, and alcoholysis lead to the degradation of polyamides and polyesters owing to scission of ester and amide linkages in presence of free carboxyl [6, 7, 8], amino [8], or hydroxyl [9] groups, and also of the ester linkages of other molecules [10]. The kinetics of these exchange reactions were studied in great detail for low-molecular-weight esters, alcohols, and acids [11].

The object of the present investigation was the experimental proof of the reaction schemes represented above for the interchain exchange processes in cases for which alcoholysis, acidolysis, and aminolysis should lead not to degradation, but to the synthesis of polyesters and polyamides having quite definite degrees of heterogeneity, corresponding to polycondensation equilibrium.

We have studied a number of samples of the synthesis of polyesters by the alcoholysis reaction. It was found, for example, that formation of polyethylene adipate proceeded readily when ethylene glycol reacted with dialkyl (dibutyl and diethyl) adipates:

$$x\,ROCO(CH_2)_4COOR + xHOCH_2CH_2OH \longrightarrow \cdots-CO(CH_2)_4CO-OCH_2CH_2O-\cdots + (2x-1)\,ROH \qquad \text{(III)}$$

This reaction proceeds more rapidly in presence of acid or alkaline catalysts, but proceeds at an appreciable rate even in their absence. We obtained a polymer of this type also by prolonged heating of bis(2-hydroxyethyl adipate:

$$x\,HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH \rightleftharpoons \cdots-OCH_2CH_2O-CO\,(CH_2)_4CO-\cdots + x\,HOCH_2CH_2OH \qquad \text{(IV)}$$

The interaction of polyester chains among themselves was verified by us also by studying the fractional composition of polyesters obtained by different methods. One of these (Sample No. 30) was prepared by heating adipic acid with ethylene glycol under the usual polycondensation conditions. The other (Sample No. 31) was prepared by prolonged heating (42 hours) of a narrow fraction of Sample No. 30 having a molecular weight of 1100.

Both polyester samples were separated into narrow fractions by a fractional-precipitation method [12]. The figure shows the molecular-weight distribution curves for Samples No. 30 and 31 of polyester. It will be seen that the distribution curves of the two samples are similar to each other, , in spite of the fact that Sample No. 30 was obtained by the polycondensation of the original substances, and Sample No. 31 was formed as the result of interchain exchange within a narrow fraction of the polymer (indicated on the figure by broken lines). The shift that has occurred in the maximum is to be explained by an increase in the degree of completeness of the reaction. The reaction of interchain exchange leads, therefore, to formation of a polycondensate having a degree of polydispersity corresponding to a state of equilibrium.

Alcoholysis of polyamide chains by hydroxy compounds does not occur in absence of catalysts. This is confirmed by the fact that prolonged heating of the diamide of adipic acid with ethylene glycol under polycondensation conditions does not lead to polyester formation. On the other hand, aminolysis of ester linkages occurs readily and leads to the formation of polyamides. We established this fact by studying the reaction of dibutyl adipate with 1,6-hexanediamine. When 1,6-hexanediamine is heated with excess of dibutyl adipate, the formation occurs of polyamides having butoxyl end groups:

$$(x+1)C_4H_9O-CO(CH_2)_4CO-OC_4H_9 + xH_2N(CH_2)_6NH_2 \longrightarrow$$

$$\longrightarrow C_4H_9O-CO(CH_2)_4CO-[NH(CH_2)_6NHCO(CH_2)_4CO]_xOC_4H_9 + 2C_4H_9OH \qquad \text{(V)}$$

Polyamide synthesis by acidolysis of amide linkages proceeds readily in absence of a catalyst. Thus, when N, N-hexamethylenebisacetamide is heated with adipic acid under polycondensation conditions, polyhexamethyleneadipamide is formed with elimination of acetic acid:

$$xCH_3CO-NH(CH_2)_6NH-COCH_3 + xHOCO(CH_2)_4COOH \rightleftharpoons \cdots-NH(CH_2)_6NH-CO(CH_2)_4CO-\cdots + (2x-1)CH_3COOH \qquad \text{(VI)}$$

Interchain exchange by the transamidation reaction (Equation IIa) proceeds rapidly only in presence of a catalyst. We have found that diethyl adipate does not react with N,N'-hexamethylenebisacetamide at 200-210° under the usual polycondensation conditions, but in presence of an aqueous solution of p-toluenesulfonic acid reaction occurs under the same conditions with formation of a polyamide and elimination of ethyl acetate.

EXPERIMENTAL

Synthesis of Bis(2-hydroxyethyl) Adipate

A mixture of 7.2 g (0.05 mole) of adipic acid and 17.4 g (0.28 mole) of ethylene glycol was heated under polycondensation conditions for nine hours at 180°. Samples were taken at known intervals of time and their carboxyl contents were determined. Reaction was discontinued when 99.5% of the carboxyl groups had entered into reaction. A mixture of water and glycol (3.4 g) was driven off, and then at 150° 8.0 g of distillate was obtained at a pressure of 2 mm. The total amount of distillate was 11.4 g, of which 1.8 g was water and 9.6 g was unchanged ethylene glycol, b.p. 195-196°. The residue in the flask (11.5 g) was a viscous liquid that did not boil under reduced pressure (2 mm) when heated to 250°. It was difficultly soluble in benzene, but readily soluble in alcohol.

The product (10 g) was dissolved in alcohol (30 ml), and the solution was diluted with water (100 ml). An oily layer of polyester formed at the top, and it was poured off; it solidified to a white greasy substance, m.p. 26-29° (1.1 g). The aqueous-alcoholic solution was evaporated to constant weight at 10 mm and 56°.

Found %: H 7.35, 7.40; C 51.61, 54.68
$C_{10}H_{18}O_6$. Calculated %: H 7.73; C 51.27
Acid number 1.5.

Determination of hydroxyl groups by Verley's method [3]:

In a control experiment 20 ml of the acetylating mixture required 35.2 ml of 0.1 N alkali (factor 1.05). In a determination on 0.1692 g of the substance 22.26 ml of alkali was required. In a determination on 0.1748 g of the substance 21.0 ml of alkali was required. These figures yield molecular weights of 226 and 230 respectively.

Found: M 230
$C_{10}H_{18}O_6$. Calculated: M 232

The product therefore corresponds in elementary analysis and molecular weight to bis(2-hydroxyethyl) adipate.

Alcoholysis of Esters

Synthesis of a polyester from bis(2-hydroxyethyl) adipate. The bis (2-hydroxyethyl) ester (7 g) was heated under polycondensation conditions for four hours at 180° and 10-12 mm. During the heating a heavy liquid slowly distilled over; it was found to be ethylene glycol (1.7 g). The residue solidified to a hard white mass, m.p. 38-40°. Viscosity measurements in benzene solution(8.6 g/ liter): η_{sp} 0.084; $[\eta]$ 0.0097; M 1800.

Reaction of diethyl and dibutyl adipates with ethylene glycol. Equimolecular amounts of dialkyl adipate and ethylene glycol were heated together under polycondensation conditions both with and without catalysts.

p-Toluenesulfonic acid and sodium ethoxide were used as catalysts (1% on the total weight of the original substances). The amount of alcohol that separated in the course of the reaction was determined by trapping it in a graduated receiver followed by tubes containing freshly calcined calcium chloride. The losses of alcohol in the apparatus, as determined by checks on pure alcohol, were 0.05 - 0.06 g. The results of the experiments are given in Table 1.

TABLE 1

Synthesis of Polyesters from Dialkyl Adipates and Ethylene Glycol

Expt. No.	Starting substances		Reaction conditions		Degree of completion of reaction	Mol. wt.*	Notes
	Amt. of ethylene glycol (g)	Amt. of ester (g)	temp. (°C)	time (hr)			
1	5.0	Diethyl adipate 16.2	160-90	5	0.32	460	No catalyst
2	3.25	" " 10.6	160-90	5	0.63	900	1% p-toluenesulfonic acid
3	3.1	" " 10.1	170-95	7	0.73	1260	1% sodium ethoxide
4	3.1	" " 10.1	160-95	6	0.73	1250	Ditto
5	3.1	Dibutyl adipate 12.9	180-200	6	0.50	700	Ditto

Aminolysis of Esters

Reaction of dibutyl adipate with 1,6-hexanediamine. A mixture of 4.6 g (0.01 mole + 75% excess) of dibutyl adipate and 1.16 g (0.01 mole) of 1,6-hexanediamine was heated in a Claisen flask for three hours at a bath temperature of 225-230°. Reaction began at 180°, and distillation of butyl alcohol had practically ceased after three hours. The temperature rose to 225° during the first hour. The distillate (1 g) consisted of butyl alcohol containing a certain amount of free base, which was determined by titration with sulfuric acid in presence of Methyl Orange. The amount of 0.1 N sulfuric acid required was 0.6 ml per g; the amount of diamine in the distillate was 0.007 g, i.e. 0.6% of the diamine taken.

The reaction product was a white, amorphous mass, m.p. 190-200°, insoluble in water and ether. Boiling absolute methanol dissolved about 40% of the total amount. The residue was soluble only in phenols and formic acid, and was precipitated from them by alcohol and water respectively. M.p. 205-207°.

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* The viscometric molecular weight was determined in all cases on samples that had been washed with water, washed with ether, and dried to constant weight. The viscosity measurements were carried out on benzene solutions.

Found %: N 9.04; 8.89

$C_{50}H_{92}O_{10}N_6$. Calculated %: N 8.98

Found %: H 10 31; 10.22; C 63.95; 63.93

$C_{50}H_{92}O_{10}N_6$. Calculated %: H 9.92; C 64.05

The molecular weight according to the elementary composition was 936, and as determined from the viscosity of a solution in m-cresol, 1000. According to its elementary composition, therefore, the product corresponded to a polyamide containing 3 residues of 1,6-hexanediamine, 4 adipic acid residues, and 2 butoxyl groups, i.e., to a polyamide having a degree of polycondensation of 7.

When the alcoholic extract of the reaction product was cooled, a white, amorphous precipitate formed, which melted, after recrystallization from 95% alcohol, at 108-112°. Repeated recrystallization from alcohol had no effect on the melting point.

Its mean molecular weight by the formula was 585. Its molecular weight determined from the viscosity of its solution in m-cresol was 630.

Acidolysis of Amides

Reaction of N,N'-hexamethylenebisacetamide with adipic acid. A mixture of 4 g (0.02 mole) of N,N'-hexamethylenebisacetamide (m.p. 124-125°) and 2.93 g (0.02 mole) of adipic acid was heated in a Claisen flask in an atmosphere of dry nitrogen (purified from oxygen) for two hours at 180° and two hours at 210-215°. During the reaction 0.25 g of acetic acid was distilled off. The residue in the flask rapidly solidified to a white mass, m.p. 145-147°. After being ground, repeatedly washed with water, and then dried, the product (4.6 g of white powder) melted at 242-245°. In admixture with polyhexamethyleneadipamide it melted at 243-246°. Its specific viscosity at 7.2 g per liter was 0.16; molecular weight 2600.

Reaction of N,N'-hexamethylenebisacetamide with diethyl adipate. 1) A mixture of 3.4 g of N,N'-hexamethylenebisacetamide (m.p. 124-125°) and 3.5 g of diethyl adipate (b.p. 102-104°/3 mm; acid number 0.004) was heated in a current of nitrogen for four hours at 200-210°. There was a partial darkening of the reaction mixture. Nothing condensed in a receiver provided, but an odor of acetic acid could be detected. The loss in weight of the reaction mixture was 0.1 g. The product melted at 110-116°; recrystallization from dry benzene yielded 3.1 g of a white crystalline substance, m.p. 124-125°. In admixture with the original N,N'-hexamethylene-bisacetamide it melted at 124-125°.

2) The experiment was repeated, but before the heating a solution of 0.1 g of p-toluenesulfonic acid in 1 ml of water was introduced into the reaction flask. During the reaction 1.4 g of a liquid smelling of ethyl acetate distilled over, but it did not separate from the water as a layer. The residue in the flask was a hard, white substance, m.p. 140-150°. Repeated washing with water yielded 3.5 g of a white powder, m.p. 244-247°, which appeared to be polyamide, but which was not investigated further.

Amide-alcoholysis reaction. The diamide of adipic acid, dried to constant weight (14.4 g, i.e. 0.1 mole; m.p. 220°) was placed in a round-bottomed flask, and 31 g of carefully dried ethylene glycol was added. The mixture was heated under reflux for three hours at 200°, and was then cooled. Absolute alcohol (50 ml) was added, and the precipitate that formed was separated, washed on the filter with absolute alcohol, and dried to constant weight (14.1 g; m.p. 219-220°). In admixture with the original diamide it melted at 219-220°.

Synthesis of Polyester No. 30

A mixture of 58.0 g of adipic acid and 24.8 g (1% excess over equimolecular amount) of ethylene glycol was heated in a current of dry nitrogen for 6 hr. 20 min. at 160° and 1 hr. 30 min. at 180°. In the course of the reaction 12.5 g of water distilled off. The residue in the flask was a white solid, m.p. 40-41°, 70 g; it dissolved readily in benzene, chloroform, and dioxane. The degree of completion of the reaction, according to the amount of water separated, was p = 0.87. The molecular weight according to the water liberated, was 770, and according to cryoscopic determination in benzene solution, 730. The specific viscosity of a benzene solution of concentration 10.32 g per liter was 0.0575. The viscometric molecular weight was 1070.

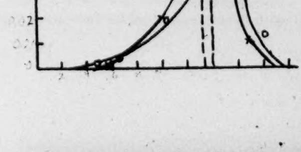

TABLE 2

Fractional Composition of Polyester No. 30

Fraction No.	Weight of fraction (g)	Losses (g)	Total weight (g)	Molecular weight
I	0.98	0.19	1.17	1430
II	1.25	0.19	1.44	1260
III	1.18	0.28	1.46	1220
IV	3.25	0.66	3.91	1120
V	1.43	0.34	1.77	860
VI	0.16	–	0.16	500
Not fractionated	8.25	1.66	9.91	1070
Calculated mean*	–	–	–	1130

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* Calculation of the mean molecular weight of the unfractionated mixture was performed by the formula $M_m = \Sigma f_x M_x$, where f_x is the proportion by weight of a fraction, and M_x is the molecular weight of this fraction.

Fractionation of Polyester No. 30

1. The polyester (10 g) was dissolved in 500 ml of dry benzene, and by fractional precipitation by means of light petroleum ether, six fractions were separated by the method described previously [12]. The results of the fractionation are given in Table 2 and in the figure.

2. Polyester No. 30 (47 g) was separated into fractions by the method indicated above. One of these fractions (16 g), which had a molecular weight of 1100, was again treated to free it from low- and high-molecular weight polymer, and the fraction so obtained (10.85 g) had a mean molecular weight of 1100.

Further attempts to separate low- and high-molecular weight impurity from this fraction were without result.

Preparation of Polyester No. 31

The fraction of polyester No. 30 having a molecular weight of 1100 (10.15 g) was heated in a sealed tube at 170° for 42 hours. In external appearance the reaction product did not differ from the original polyester.

Some of the polyester so obtained (9.5 g) was dissolved in 500 ml of benzene, and six fractions were separated by fractional precipitation with petroleum ether. The results are given in Table 3. The curve for the distribution of fractions of different molecular weights is given above in the figure.

TABLE 3

Fractional Composition of Polyester No. 31

Fraction No.	Weight of fraction (g)	Losses (g)	Total weight (g)	Molecular weight
I	1.10	0.28	1.38	1550
II	1.22	0.23	1.45	1320
III	1.33	0.19	1.52	1290
IV	3.06	0.57	3.63	1150
V	0.89	0.34	1.23	750
VI	0.17	–	0.17	450
Not fractionated	7.77	1.61	9.38	1200
Calculated mean	–	–	–	1190

SUMMARY

1. A study has been made of interchain-exchange reactions, leading to the synthesis of polyesters and polyamides, in compounds having amide and ester linkages.

2. It has been shown that, in presence of free hydroxyl, carboxyl, or amino groups, exchange reactions of the alcoholysis, acidolysis, or aminolysis types respectively occur at ester linkages. Amide linkages are broken only by amino and carboxyl groups; they are stable toward hydroxyl groups.

3. It has been found that no exchange reaction occurs between diethyl adipate and N,N'-hexamethylenebisacetamide in absence of catalyst; it occurs only in presence of an acid catalyst.

4. It has been shown that a narrow fraction of a polyester undergoes considerable change when subjected to prolonged heating: interchain exchange reactions occur, resulting in the formation of a more heterogeneous material, the distribution curve for which is similar to that of the original unfractionated polyester obtained by the polycondensation of adipic acid with ethylene glycol.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 59. STEREOCHEMISTRY OF α-METHYLSTYRENES IN ITS RELATION TO THEIR TENDENCY TO UNDERGO POLYMERIZATION

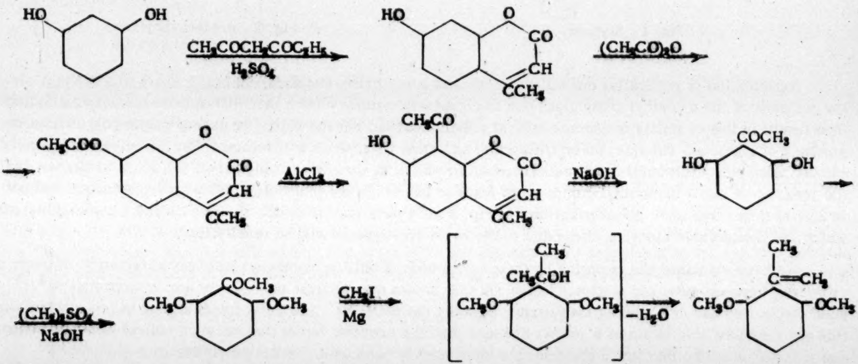
V. V. Korshak and N. G. Matveeva

As we have shown in the preceding communication, meta and para substituents in the styrene molecule have no steric-hindrance effect on the polymerization process; this is true also for a single substituent ortho to the vinyl group [1]. Even such a large substituent as the isopropyl group — as shown, for example, by the behavior of the 2,4,5-triisopropylstyrene that we prepared [1] — does not impede polymerization. But if there are two ortho substituents, the effects are much greater. We found that the nature of these substituents was important also. Thus in the case of the methoxyl group (2,6-dimethoxystyrene [1]), the ease of rotation and the small size of the oxygen atom results in an absence of steric hindrance, and this styrene derivative readily polymerizes; but the behavior of 4-tert-butyl-2,6-dimethylstyrene [2] shows that when the substituent is a methyl group great steric difficulties arise in the process of radical polymerization, which is practically inhibited, although the styrene derivative is still able to undergo ionic polymerization.

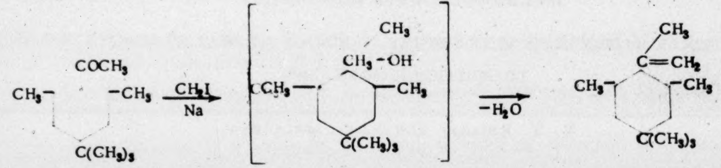
It was of great interest to consider the steric effects in ortho-disubstituted styrenes in their relation to the effects of substituents in the vinyl group. We have previously studied some unsymmetrical disubstituted ethylenes, and have shown that steric hindrance is considerable only for such large substituents as phenyl and cyclohexyl [3].

In this investigation we have studied the stereochemical effects occurring in certain 2,6-disubstituted α-methylstyrenes. For this purpose we synthesized 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene and investigated their ability to undergo polymerization. 2,6-Dimethoxy-α-methylstyrene was prepared by a long succession of reactions, which are shown schematically below.

The starting substance was 4-methylumbelliferone, which was prepared from resorcinol and acetoacetic ester in presence of concentrated sulfuric acid. Acetylation of 4-methylumbelliferone, Fries rearrangement, and hydrolysis of the product led to 2',6'-dihydroxyacetophenone, which was methylated with dimethyl sulfate, yielding 2',6'-dimethoxyacetophenone. This was converted by the action of methylmagnesium iodide into 2,6-dimethoxy-α,α,-dimetheybenzyl alcohol, which immediately underwent dehydration, yielding 2,6-dimethoxy-α-methylstyrene, a liquid of b.p. 136-138° at 26 mm.



4-tert-Butyl- α-,2,6-trimethylstyrene was prepared from 4'-tert-butyl-2',6'-dimethylacetophenone by the following reactions:



Treatment of 4'-tert-butyl-2',6'-dimethylacetophenone with methyl iodide and sodium (Shorygen's reaction [5]) 4-tert-butyl-α,α,2,6-tetramethylbenzyl alcohol, which underwent dehydration in the course of isolation, yielding 4-tert-butyl-α,2,6-trimethylstyrene, a liquid of b.p. 124—125°/3 mm. Our attempts to prepare this substance with the aid of methylmagnesium iodide were not successful, for it was found that 4'-tert-butyl-2',6'-dimethylacetophenone did not react with methylmagnesium iodide and could be recovered unchanged after the treatment. It was thus possible to overcome the steric hindrance in this reaction only with the help of Shorygin's reaction.

The α-methylstyrenes obtained were submitted to various treatments in a search for ways of bringing about their polymerization. They were heated at 200° for 250 hours; heated for a long time in presence of benzoyl peroxide; subjected to the action of aluminum chloride; and irradiated for a long time with ultraviolet radiation from a quartz lamp. In no case, however, was any sign of polymerization detected. We were therefore forced to the conclusion that these α-methylstyrenes are completely unable to undergo polymerization

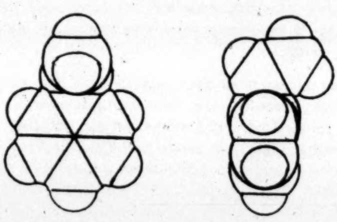


Fig. 1. Styrene.

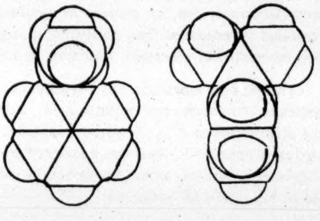


Fig. 2. α-Methylstyrene.

Examination of the spatial models of styrene and α-methylstyrene shown in Fig. 1 and 2 will make it clear that the presence of the α-methyl group gives rise to considerable steric effects that will impede the polymerization process. This results in loss of ability to undergo radical polymerization, but the ability to undergo ionic polymerization in presence of aluminum chloride, boron trifluoride, and other catalysts is still retained. In this respect α-methylstyrene closely resembles 4-tert-butyl-2,6-dimethylstyrene, in which, as we have already shown [2], steric hindrance due to the presence of two ortho-methyl groups again leads to loss of ability to undergo radical polymerization without loss in ability to undergo ionic polymerization. In Fig. 3 we show a spatial model of 4-tert-butyl-2,6-dimethylstyrene in which the considerable blocking effect due to the two methyl groups will be readily seen.

We have explained the retention by these compounds of ability to undergo ionic polymerization in terms of the difference between polar and nonpolar forces, for it is known that whereas polar forces are proportional to $^{1}/r^{3}$, nonpolar forces vary as $^{1}/r^{10}$, *r* being the distance between the particles The polar forces arising in ionic polymerization are therefore able to act at a greater distance than the nonpolar forces that occur in radical polymerization, and it is not surprising that steric obstacles are more readily overcome in ionic polymerization [2].

When we compare these two compounds with the two compounds that we have now synthesized, 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene, spatial models of which are represented in Fig. 4 and 5, it is readily seen that in these compounds the steric hindrance has increased many times. This arises from the superposition of the screening and blocking effects arising from the two substituents As a result, the steric obstacles

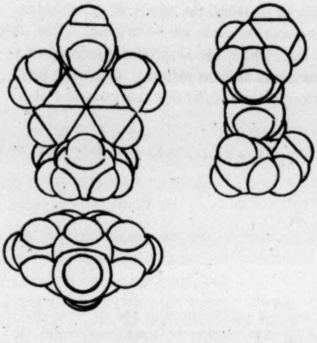


Fig. 3. 4-tert-Butyl-2,6-dimethylstyrene.

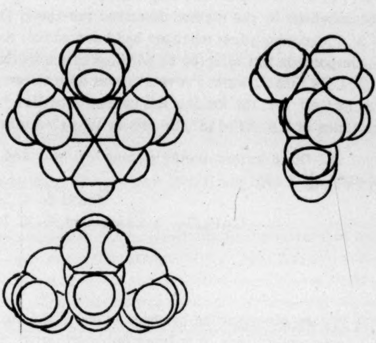


Fig. 4. 2,6-Dimethoxy-α-methylstyrene.

become so great that they inhibit reaction not only with free radicals, but also with the ions present during ionic polymerization.

We may therefore conclude, on the basis of the behavior of these two ortho-substituted α-methylstyrenes, that even a small substituent, such as a methyl group, can create very great steric obstacles to the polymerization of disubstituted ethylene, when the second substituent is ortho-disubstituted phenyl. It follows that, as we have previously shown, stereochemical factors may hinder the polymerization not only of tetrasubstituted ethylenes [4] and of disubstituted ethylenes having two large substituents [3], but also of disubstituted ethylenes having one small and one large, ramified substituent.

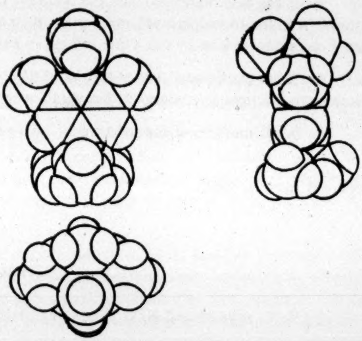


Fig. 5. 4-tert-Butyl-α,2,6-trimethylstyrene

EXPERIMENTAL

4-tert-Butyl-α,2,6-trimethylstyrene. 4'-tert-Butyl-2',6'-dimethylacetophenone (100 g), methyl iodide (210 g), and granulated sodium (48 g) in ether (250 ml) were introduced into a round-bottomed flask fitted with reflux condenser. As the beginning of the reaction was generally somewhat delayed, ethanol (1 ml) was added as primer. When reaction began to die down, the flask was heated in a water bath for one hour; it was then set aside overnight. The ether layer, containing suspended alkoxide, was carefully decanted from the sodium, and the residual sodium was shaken several times with ether, the ethereal suspension of alkoxide being poured off each time. The ether extracts were united, and the alkoxide was decomposed with water. The ether layer was separated in a separating funnel and then washed, first with water, then with dilute hydrochloric acid, and then again with water. The washed ether layer was dried with calcined sodium sulfate, the ether was distilled off, and the residue was vacuum-distilled. After three distillations 15.7 g (15.5%) of a substance of b.p. 124—125°/3 mm was obtained.

4-tert-Butyl-α,2,6-trimethylstyrene is a colorless viscous oil having an odor of turpentine; d_4^{20} 0.9489; n_D^{20} 1.5050; found MR 68.13. Calc. Mr. 68.62. It is readily soluble in organic solvents and insoluble in water.

Found %: C 88.20, 88.22; H 10.58, 10.61
Calculated %: C 89.03; H 10.96.

2,6-Dimethoxy-α-methylstyrene. Magnesium turnings (1.32 g) were placed in a two-necked flask fitted with a reflux condenser and dropping funnel, and a mixture of methyl iodide (12 g) and absolute ether (50 ml) was added from the funnel. When the magnesium had dissolved, a solution of 2',6'-dimethoxyacetophenone (10 g) in absolute ether (50 ml) was added (2',6'-dimethoxyacetophenone was prepared from 2',6'-dihydroxyacetophenone by the method described previously [1]; it boiled at 69-70°). When the whole of the solution of 2',6'-dimethoxyacetophenone had been added, the reaction mixture was set aside for 30 minutes, after which decomposition was effected by addition of ammonium chloride solution. The ether layer was separated in a separating funnel, washed several times with water, and dried with calcined sodium sulfate. The ether was distilled off, and the residue was vacuum-distilled. After three distillations 4.7 g (47.6%) was obtained of a substance of b.p. 136-138°/26 mm or 92-94°/3 mm.

2,6-Dimethoxy-α-methylstyrene was obtained in the form of clear crystals having an aromatic odor, m.p. 36-37°, d_4^{18} 1.043.

Found %: C 74.30, 74.55; H 8.16, 8.18.
$C_{11}H_{14}O_2$. Calculated %: C 74.13; H 7.92.

SUMMARY

1. An investigation has been made of the ability of 2,6-dimethoxy-α-methylstyrene and of 4-tert-butyl-α,2,6-trimethylstyrene to undergo polymerization, and it has been found that neither of these compounds is able to polymerize.

2. It has been suggested that the inability of 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene to undergo polymerization is to be explained by stereochemical considerations, namely by the steric obstacles created by the α-methyl group and the two ortho-substituents.

3. It has been found that 4'-tert-butyl-2',6'-dimethylacetophenone does not react with organomagnesium compounds, but readily undergoes Shorygin's reaction with organosodium compounds.

4. 2,6-Dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene have been synthesized.

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* See Consultants Bureau Translation, p. 487.
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CHRONICLE

AT THE COMMITTEE FOR THE INVESTIGATION OF THE SCIENTIFIC HERITAGE OF D. I. MENDELEEV AND THE PUBLISHING OF HIS WORKS

In Leningrad on February 12th and 13th, 1953, there was a scientific session of the committee for the investigation of the scientific heritage of D. I Mendeleev and the publishing of his works, which was held conjointly with the Leningrad section of the D. I. Mendeleev Chemical Society.

In his introductory address, Academician A. V. Topchiev remarked that in recent years a considerable number of D. I. Mendeleev's works and collections of papers throwing light on various aspects of the great Russian scientist's activities had been published, but it had to be acknowledged that we have not yet published an adequate number of his works and have not done enough toward their popularization. The position was particularly unsatisfactory with respect to the study of the D. I. Mendeleev archives and the publication of documents to be found there will form an important supplement to the published works of D. I. Mendeleev.

Academician A. V. Topchiev pointed out that, at the present time, the main problem of those investigating D. I. Mendeleev's works was the sorting out of his archives and the deciphering and study of the manuscripts. It was quite to be expected that all the reports read at these sessions of the committee would contain much new material found in the D. I. Mendeleev archives.

Now that all documents left after D. I. Mendeleev's death were concentrated in one place—the D. I. Mendeleev Archive-Museum at the A. A. Zhdanov University of Leningrad, the work of those investigating D. I. Mendeleev's works had been considerably lightened.

In an extensive report, "The Contribution of D. I. Mendeleev to Petroleum Science", Academician A. V. Topchiev drew a clear, vivid picture of the scientific, organizational, and technological activities of Mendeleev in the petroleum field. The large amount of archive material cited enabled a fuller picture of the actions and thoughts of the great Russian chemist to be obtained.

Already on his first acquaintance with the Baku petroleum establishments in 1863, Mendeleev made a number of suggestions that would permit an improvement in the technique of petroleum treatment, but his main attention, even at that time, turned to the necessity for the construction of petroleum pipe-lines. Archive material that has recently been found shows that in 1863 Mendeleev not only came to realize the necessity for the establishment of plants for the treatment of petroleum in the center of Russia, but also decided to take upon himself the technical direction of a plant which was to be constructed near Nizhny Novgorod. The various notes, plans, and texts of agreements with the petroleum industrialist V. A. Kokarev show the detailed manner in which D. I. worked out all the technological processes for the treatment of petroleum, into which he introduced many new features, and the great amount of attention he gave to the question of the transport of petroleum along the Volga, for which he proposed the use of tankers of his own design. All these documents characterize D. I. Mendeleev as a technologist.

Already in the first stages of his activities in the petroleum field, Mendeleev realized the enormous importance of scientific investigation. "Without science our work with petroleum will be in the dark", he said.

Academician Topchiev cited a large amount of archive material showing the extensive researches carried out by Mendeleev in the course of his studies of the composition of petroleums and their physical and chemical properties. The notebooks found in the Mendeleev Archives at Leningrad University have yielded some extremely important material, supplementary to D. I. 's published work on the investigation of petroleum. Thus, Mendeleev, using a pycnometer of his own design, determined with great accuracy the specific gravities of various petroleum fractions; also their coefficients of expansion. He carried out some investigations, very interesting both from the theoretical and the practical point of view, on the purification of petroleum products by the aid of chemical reagents; he examined the action on petroleum of various acids, ammonium chloride, and ammonia, and used as purifying agents fuller's earth, charcoal, pumice, and broken brick. In a study of the oxidation of petroleum products by atmospheric oxygen, Mendeleev showed that it was possible to separate the heavy fractions from petroleum by the action of selective solvents.

Academician A. V. Topchiev brought forward much material to show the steadfastness and inventiveness exhibited by Mendeleev in his efforts to achieve better fractionation of the petroleum by the aid of fractional distillation. Mendeleev constructed several pieces of apparatus in which he was able to separate the petroleum into two-degree fractions. Great interest was aroused by the photographs shown by Academician Topchiev of graphs from Mendeleev's notebooks; on these the ordinates were the mean boiling points of the fractions and the abscissae were their specific gravities. Mendeleev established that the specific gravity curve for petroleum is characterized by alternate minima and maxima, and he suggested on the basis of this fact that the petroleums studied contained at least two types of hydrocarbons, the lighter being saturated, and the heavier unsaturated. Academician Topchiev particularly emphasized that these conclusions, so important from the chemical point of view, were arrived at by Dmitry Ivanovich on the basis of purely physical and physicochemical methods of investigation. Now that he had exact methods for the characterization of petroleum at his command, D. I. Mendeleev was able to establish that the chemical composition of petroleum depends on the conditions of its geological occurrence.

Mendeleev persistently urged industrialists to improve their methods of treating petroleum, to use continuous methods of distillation, and to employ fractionation columns. While working in 1881 at the Konstantin works near to Yaroslavl, Mendeleev tried out new methods of distilling petroleum and a new, improved distillation plant, made to his design, under works conditions. Mendeleev was interested in the thermal treatment of petroleum—what was subsequently to be called "cracking".

Much interesting information was given by Academician Topchiev concerning the way D. I. Mendeleev strove for the full utilization of all of the substances found in petroleum. Mendeleev showed how extremely valuable petroleum is in the national economy and was the first to do so; and he was the first to proclaim, as he did in his papers and speeches, the necessity for the full processing and rational utilization of petroleum. At the beginning of the eighties, Mendeleev pointed out the possibility of obtaining aromatic hydrocarbons and organic dyes from petroleum. Owing to Mendeleev's persistence, valuable lubricating oils started to be produced in Russia, and kerosene (which was called photonaphthyl in the middle of the nineteenth century) was obtained in quantities that permitted not only the cessation of the importation of kerosene from America, but also its export to other countries. Mendeleev devoted much effort to the development of a method of preparing a safe illuminating oil, which he called bakuol. He took an active part in a competition for a safety lamp.

Only under the conditions of Soviet rule has Mendeleev's dream about petroleum come true. His desire that petroleum should be obtained in the island of Cheleken, in the north of Russia, and in the Povolzhy provinces has been fulfilled, and Mendeleev's prophetic words about petroleum as a raw material for the preparation of chemicals have come true.

In conclusion, Academician A. V. Topchiev pointed out that the rich scientific heritage of D. I. Mendeleev in petroleum science and industry has not yet been developed to the extent that it should be. The numerous notebooks, record books, and separate notes by D. I. Mendeleev preserved in the scientific archives at the A. A. Zhdanov University of Leningrad conceal many ideas that can fertilize the creative thought of Soviet investigators. Careful study and development of the scientific heritage of D. I. Mendeleev will help Soviet petroleum scientists in their persistent every-day work on the study of the composition, properties, and treatment of petroleum with the object of solving the problem of the rational utilization of petroleum in accordance with the historic resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union.

In connection with Academician Topchiev's report, the library of the USSR Academy of Sciences opened an exhibition entitled D. I. Mendeleev and the Russian petroleum industry". The exhibition, which aroused great interest, consisted of six sections:

1. Information about petroleum in the Russian literature of the eighteenth century.
2. The petroleum industry in Russia before Mendeleev.
3. D. I. Mendeleev's work on petroleum.
4. The petroleum industry in Russia from Mendeleev to the Great October Socialist Revolution.
5. The petroleum industry in the Soviet Union.
6. Innovators in the petroleum industry.

Some of the staff of the Reference and Bibliographical Section of the library of the USSR Academy of Sciences—L. M. Garkavi, N. N. Deikova, and O. P. Kamenogradskaya—organized the exhibition and were able to exhibit many little-known works.

A noteworthy exhibit in the first section was a copy of "Vedomosti" ("The News"), issue No. 1 of 1703, in which there is a note entitled "News of the Presence of Petroleum in Kazan". Works by M. V. Lomonosov, F. P. Soimonov, I. Lepekhin, and other authors of the eighteenth century, which contain information concerning the occurrence of petroleum in Russia, were also worthy of note.

A particularly rich display of material was to be found in the section entitled "The petroleum industry in Russia from Mendeleev to the Great October Socialist Revolution". Here visitors to the exhibition saw the works of M. I. Konovalov., K. V. Kharichkov, V. V. Markovnikov, A. A. Letny, K. Lisenko, A Kurbatov, and others.

The petroleum industry in the Soviet Union was represented by the works of the great Soviet academician-scientists—Gubkin, Zelinsky, Nametkin, Topchiev, and others—and also by numerous works by innovators in the petroleum industry.

Altogether, 160 books were exhibited.

The work of D. I. Mendeleev leading up to the discovery of the periodic law was the subject of an address by Prof. B. M. Kedrov. The speaker made an analysis of a number of recently discovered items by Mendeleev which show how the discovery of the great natural law came about. These items may be conveniently divided into three groups. The first group comprises documents of the earlier years of Mendeleev's scientific work (1856-1867)—from the time when he left the Chief Padagogical Institute to the date of his acceptance of the chair of chemistry in St. Petersburg University. These investigations include those on isomorphism, specific volumes, the theory of limits, etc., and they disclosed the relations between the elements which were later (1869) advanced in the form of physical and chemical functions of the atomic weights. Particular significance is to be attached to those items that indicate the way in which Mendeleev studied the problem of the determination of atomic weights and the distribution of elements into "natural groups".

The second group of items contains Mendeleev's notes in connection with his lectures at St. Petersburg University and with the composition of the first part of the "Principles of Chemistry" and the planning of the second part (from the end of 1867 to the beginning of 1869). This material led directly to the discovery of the periodic law, which occurred during work on the "Principles of Chemistry", as stated on several occasions by Mendeleev himself.

The third group of items comprises documents to which the date of the actual discovery—17th February 1869 (Old Style)—must be assigned. On that day Mendeleev had arranged to go out on a mission for the Free Economic Society, but he evidently did not go out, owing to his work on the first variants of the periodic system. Five documents are to be assigned to that day, and three of them, which are dated 17th February 1869, permit us to determine the moment of the beginning of the discovery and the moment of its completion during the course of that day, and also the course of this discovery as it became manifested in an ever fuller and deeper revelation of the relations between individual elements and whole groups of elements and in the embracing by the system of an ever increasing number of elements, until finally it embraced all of the 63 elements known at that time.

The newly discovered material enables us to determine many important details of the history of the great discovery made by Mendeleev; in particular, it confirms the supposition that, when discovering the periodic law, Mendeleev did not arrange the elements in one general series (according to their atomic weights) and then break this down into periods, but arranged them in groups in such a way that one group of elements was written below another in accordance with the atomic weights of their members.

B. M. Kedrov stated that all this material, and also Mendeleev's notes on his laboratory experimental investigations on chemistry carried out in 1869—1871, would be included in the second volume of the "Scientific Archives of D. I. Mendeleev", now in preparation; this, like the first volume of this series, is to be devoted to the periodic law.

In a report on "The Manuscripts of D. I. Mendeleev on the Theory of Limits", P. B. Dobrotin, a member of the staff of the Mendeleev Archives, gave some interesting information on Mendeleev's preparatory work on his theory of the limits of organic compounds. These manuscripts, now studied for the first time, belong to the year 1861, and in these can be seen, much more clearly than in the printed articles, the precursory thoughts and basic ideas leading Mendeleev to the finished theory of limits, which was expounded in special articles and in the book "Organic Chemistry".

The speaker considered that in his theory of limits Mendeleev expressed a view on chemical compounds that was very progressive at that time. D. I. Mendeleev, although not yet employing any scheme of valency distribution, clearly understood the possibility of learning the mutual influence of atoms in a molecule, thus completely refuting the theory of types. Simultaneously with the theory of limits, D. I. Mendeleev developed the concept of the forms of compounds. Both of these concepts (limits and forms) played a foremost part in the further work of D. I. Mendeleev and must be regarded as important stages on the road to the discovery of the periodic law.

The former personal secretary of the great Russian scientist, Aleksei Vasilyevich Skvortsov, shared with us some of his wide experience in the deciphering of Mendeleev's handwriting in the paper he gave entitled "Transcription of D. I. Mendeleev's manuscripts and their deciphering". Mendeleev's handwriting was distinguished by many peculiarities that make it not readily accessible to the reader. Thus, D. I., trying to put on paper the thoughts that came too fast for his pen, often abbreviated words and ran several words together.

A. V. Skvortsov showed by a number of examples the characteristic ways used by Mendeleev for the abbreviation of words and of combinations of groups of words. A great amount of practice is necessary in order to get used to these peculiarities in Mendeleev's writing. The speaker showed a large number of photographs of individual pages from the notebooks and diaries of Mendeleev and indicated how individual letters were written. The letters "Ya", "T", and "K" are particularly difficult to read; it is interesting that Mendeleev wrote the combination of the letters "c" and "t" as if it were the letter "b".

As a result of a great deal of hard work, A. V. Skortsov has deciphered thirty-two notebooks, numerous working records, diary notes, jottings, letters, etc., comprising altogether about 2000 typewritten sheets.

Newcomers, now entering upon the study of the works of our great chemist, must acquire from A. V. Skvortsov the ability to decipher D. I. Mendeleev's manuscripts.

Members of the committee visited the D. I. Mendeleev Archive—Museum, where a session was held, under the chairmanship of Academician A. V. Topchiev, relating to various questions of organization and the publishing of material.

The space available for the museum has been considerably increased. The room that was for many years Mendeleev's study now forms part of the museum, and books and other objects that were actually in Mendeleev's study during his lifetime have now been placed there.

The staff of the museum now has the great task of staging an exhibition covering all aspects of the activities of the great Russian scientist.

TO THE MEMORY OF ACADEMICIAN NIKOLAI DMITRIEVICH ZELINSKY

The death occurred on July 31, 1953, at the age of ninety-two, of the eminent chemist Academician Nikolai Dmitrievich Zelinsky, senior professor at the M.V. Lomonosov Moscow State University, Hero of Socialist Labor, recipient of three Stalin prizes, and holder of four Orders of Lenin and two orders of the Red Banner of Labor. In the person of Zelinsky Soviet science has lost a great organic chemist, founder of the science of heterogeneous organic catalysis and of petroleum chemistry, inventor of the first universal charcoal gas mask in the world, scientist of manifold activities, and teacher and trainer of several generations of chemists.

Zelinsky was the author of about six hundred original scientific papers and inventions in the fields of organic, physical, and inorganic chemistry, including petroleum chemistry and the chemistry of artificial liquid fuel. The investigations of Zelinsky and his school, the largest in the USSR on the synthesis of hydrocarbons, organic catalysis, petroleum chemistry, and protein chemistry, have occupied and continue to occupy a leading position in world science.

N. D. Zelinsky was born on February 6 (New Style), 1861, in Tiraspol in the province of Kherson (now Moldavian Autonomous SSR). At the age of two he lost his father, and a year and a half later his mother died also. He was brought up by his maternal grandmother, M. P. Vasilyeva, a good, sympathetic, cultured woman, very progressive in ideas for the time in which she lived; Zelinsky retained fond memories of her to the last days of his life. He received his early education from his grandmother, and she provided for his further education at the Rishelyevsky Gymnasium in Odessa, which he attended until 1880. While still a schoolboy, Zelinsky listened enthusiastically to the lectures of the eminent physiologist I. M. Sechenov at the university. From the gymnasium, Zelinsky passed to the Natural History Department of the Physico-mathematical Faculty of the Novorossiisky University (Odessa), which he attended until 1884. His first chemistry teachers at the university were E.F. Klimenko, A. A. Verigo, V. M. Petriev, and P. G. Melikov (Melikishvili). It was under the direction of Melikov that Zelinsky, as a student, carried out his first scientific investigation on the "Product of the Addition to Methylamine to β-Methylglycidic Acid", which was published in 1884 in the Journal of the Russian Physicochemical Society.

With regard to his first teacher, P. G. Melikov, Zelinsky wrote with great warmth of feeling in 1950: "All my life I have been constantly grateful to my teacher for the attention and cooperation that he gave to me over a period of many years"; and also "The memory of this man, who was my first teacher, I preserve as the best of my memories of my student days at the Novorossiisky University".

In biology Zelinsky's teachers included the eminent Russian scientists A. O. Kovalevsky (zoology), I. I. Mechnikov (embriology and evolutionary theory), and L. S. Tsenkovsky (botany).

Personal intercourse and friendship with his eminent teachers, and later with the giants of Russian progressive science – I. M. Sechenov, K. A. Timiryazev, P. N. Lebedev, N. A. Umov, and A. G. Stoletov – had an exceptional, favorable influence on the formation of the materialistic world-view of N. D. Zelinsky, whose interests in the future were to range over such a wide field of science, and who as a research chemist was to enter into the highest ranks of the creators of world chemical science.

Soon after completing his course at the Novorossiisky University, Zelinsky was sent as a faculty stipendiary to Germany, where he worked under the great organic chemists of that time, J. Wislicenus (Leipzig) and Prof. Victor Meyer (Göttingen), and then somewhat later, during his second visit abroad, under the famous Wilhelm Ostwald, one of the founders, after Lomonosov, of classical physical chemistry.

The investigational work carried out by the young Zelinsky under the direction of these great chemists determined, to a great extent, the three important directions of his subsequent investigations. He began some investigations, of great interest from the point of view of theory, on the chemical nature and isomerism of compounds of the thiophene series and on the stereoisomerism of carboxylic acids, and these subsequently provided valuable material for his Master's (1889) and Doctor's (1891) theses. In Ostwald's laboratory Zelinsky began his original investigations in physical chemistry and electrochemistry, and these had an important influence on his subsequent classical investigations in organic chemistry and heterogeneous catalysis.

It is worthy of note that Zelinsky, the future inventor of the charcoal gas mask, while carrying out the synthesis of the then unknown tetrahydrothiophene in Victor Meyer's laboratory at Göttingen, obtained mustard gas, i.e. bis (2-chloroethyl) sulfide, for the first time, and, not suspecting the toxicity of the intermediate product in his synthesis, became the first victim of this treacherous, poisonous substance; he had to remain in the hospital for a whole term with badly burned arms.

On returning to Odessa, Zelinsky immediately began to build up his investigational school, bringing together his first students and collaborators, among whom we may note A. A. Bychikhin (later professor at the Novorossiisky University), A. M. Bezredka (later deputy director of the Pasteur Institute in Paris), S. G. Krapivin (later second professor at Moscow State University), and A. G. Doroshevsky (later first privatdocent at Moscow State University). In the Odessa period of his activities the main attention of Zelinsky and his students was concentrated on the synthesis of many di- and tri- substituted succinic, glutaric, adipic, and pimelic acids, and also of some substituted dibasic hydroxy acids, and the investigation of the stereoisomerism phenomena exhibited by these substances. Stereochemistry was then a completely new branch of organic chemistry, and here in Russia Zelinsky was one of the first bold investigators and exponents in this fruitful field of ideas. Zelinsky's investigations on isomerism in the thiophene series and the stereoisomerism of dibasic aliphatic acids made a substantial contribution to the development of A. M. Butlerov's Theory of Chemical Structure, the secure materialistic basis of organic chemistry.

On the recommendation of D. I. Mendeleev, N. D. Zelinsky was invited in the summer of 1893 to take up the post of extraordinary professor at Moscow University in the department of analytical and organic chemistry, and from that time, and for the remainder of his life (nearly sixty years), Zelinsky carried out exceptionally valuable scientific, pedagogic, administrative, and social work within the walls of the university, as well as in the Academy of Sciences of the USSR, to which he was elected as Active Member in 1929.

In Moscow University, Zelinsky's attention gradually passed over to a new, wide, and very important field, the chemistry of alicyclic hydrocarbons, or naphthenes. Before this time remarkable investigations had been made in Russia in this direction by such eminent chemists as F. R. Wreden, F. F. Beilstein, D. I. Mendeleev, and V. V. Markovnikov. Zelinsky, however, in this field also made a path for himself, bridging over from the dibasic carboxylic acids of the aliphatic series that he had studied so thoroughly to the alicyclic systems. This bridging over was possible because of the perfection and further development by Zelinsky of Wislicenus' cycloketonization of dibasic carboxylic acids.

In the period from 1894 to 1911 Zelinsky with his students and coworkers synthesized and characterized more than forty hydrocarbons of the cyclopentane and cyclohexane series. Many of them, and many of those synthesized later in the detailed investigations made by Zelinsky into the chemical nature of Soviet Petroleum, have served as valuable standards in the establishing of the composition of narrow gasoline fractions. It should be noted that also in this new field of work much attention was given to the stereochemical side of the study of cyclic hydrocarbons.

The following investigations belong to this first period of Zelinsky's activities at Moscow University: the remarkable work on the pyrogenetic decomposition of petroleum; the beginning of the classical investigations on selective dehydrogenational catalysis, which was discovered by Zelinsky; the development of a simple method for the preparation of α-amino acids and their esters; the beginning of extensive investigations on the catalytic hydrolysis of proteins and a series of original physicochemical investigations.

N. D. Zelinsky, appreciating the high value of work by A. A. Letny on the pyrolysis of petroleum which had remained unnoticed, made a deeper study of the thermal decomposition of petroleum distillates, and by his direct participation in large-scale trials rendered great scientific and practical service in the development of the pyrolysis industry in Russia. Already in 1901 Zelinsky gave his support to the technologist Nikiforov and helped the latter to realize his project of petroleum pyrolysis at high pressure; as he was engaged in a study of the thermal decomposition of petroleum, he joined with Nikiforov in developing the first variant of the modern thermal cracking of petroleum products.

The field of Zelinsky's investigations on heterogeneous organic catalysis is so wide, and the results are so important and varied in character that we must confine ourselves to a citation of a few of the most brilliant examples, in which Zelinsky's creative talents are most clearly manifest. Thus, already in 1905, Zelinsky with his student I. Pappe effected for the first time the conversion of a cyclopentane ring into a cyclohexane ring by contact catalysis, the example investigated being the conversion of ethylcyclopentane into methylcyclohexane and toluene in presence of aluminum bromide and bromine. Later, in Zelinsky's laboratories in Moscow State University and the Academy of Science of the USSR, on the basis of this important discovery, the equilibrium reaction of enlargement of a five-membered ring was considerably improved by the use of aluminum chloride and determination of the optimum conditions. It was established by the detailed investigations of Zelinsky and his students that the content of cyclohexanes in petroleum distillates could be increased by 15—25% with the aid of this reaction.

In 1911 N. D. Zelinsky discovered the now well-known selective catalytic dehydrogenation of cyclohexanes and their functional derivatives in presence of platinum or palladium black at 300°. This remarkable reaction received further study in the later investigations of Zelinsky, working with numerous students and coworkers. In his work with G. S. Pavlov and A. A. Balandin, the kinetics of dehydrogenational catalysis were studied, and this subject was developed in detail in later investigations of A. A. Balandin, working with A. M. Rubinshtein, N. I. Shuikin, and Yu. K. Yuryev. Mainly on the basis of this extensive material, A. A. Balandin has created his well known multiplet theory of dehydrogenational catalysis.

To the same year, 1911, belongs the discovery made by N. D. Zelinsky and N. L. Glinka of the very interesting reaction of hydrogen redistribution in cyclohexenes and cyclohexadienes under the catalytic action of finely dispersed palladium or platinum, in which the corresponding cyclohexanes and aromatic hydrocarbons are formed. This conversion of labile forms to stable forms is irreversible, and for this reason Zelinsky described the phenomenon that he had discovered as irreversible catalysis. Later, these investigations were continued by Zelinsky in conjunction with B. A. Kazansky and R. Ya. Levina, and they developed the irreversible catalysis of hydrocarbons along lines peculiar to this phenomenon.

In this period Zelinsky's school grew rapidly, always exhibiting exceptional concern for the growth and training of research teams. The names of the many talented students of N D. Zelinsky speak for themselves; they included the well-known chemists A. N. Reformatsky, V. V. Rudevich, N. A. Shilov, L. A. Chugaev, A. G. Generozov, S. N. Naumov, N. A. Rozanov, I. A. Tselikov, D. K. Aleksandrov, I. F. Gutt, S. S. Nametkin, A. E. Mozer, P. P. Lebedev, V. V. Chelintsev, E. S. Przhevalsky, A. V. Rakovsky, A. N. Lebedev, G. L. Stadnikov, N. A. Izgaryshev, N. A. Shlezinger, A. Gorsky, I. V. Kulikov, A I. Annenkov, A. E. Uspensky, V. P. Kravets, B. M. Berkengeim, V. V. Longinov, N. L. Glinka, and N. I. Chervyakov. Many of them have occupied and continue to occupy important positions in the universities and have, in their turn, created their own original directions in science and their own schools of talented students. Some of Zelinsky's students, such as L. A. Chugaev and N. A. Shilov, who later became eminent scientists and took up high university appointments, in addition to their research work performed also the duties of lecture assistants to their teacher in talented fashion.

In 1911, in connection with the intensified repression by the Tsarist government of progressive university teachers and students, N D. Zelinsky decided to leave Moscow University. By a decree issued by one of the most reactionary satraps of the Imperial government, the Minister of Education L. A. Kasso, the whole presidium of Moscow University, which consisted of the progressive professors A. A. Manuilov, M. A. Menzbir, and P. A. Minakov, was dismissed. As a sign of protest Zelinsky and a large group of professors and teachers resigned. He then moved to St. Petersburg, where he took up the post of director of the Central Laboratory of the Ministry of Finances and head of the commercial department in the Economics Faculty of the Polytechnical Institute.

In St. Petersburg, Zelinsky, in spite of his bitter experiences in connection with leaving the most important chair in the oldest university in Russia and becoming separated from his large team of students, resumed his scientific investigations with his former vigor and persistence It was at this period that he carried out his extensive and original investigations in conjunction with V. S. Sadikov on the hydrolysis of proteins under pressure and began his work on the condensation of acetylene to benzene and its homologs in presence of active charcoal; in particular it was at this period that he made his unforgettable investigations on the properties of active charcoal and its use as a universal means of protection from toxic substances. Here also we must mention Zelinsky's remarkable investigations on the cracking of petroleum hydrocarbons in the presence of natural (aluminosilicates) and synthetic oxide catalysts, which thus anticipated Houdry's invention by more than 20 years. Already in 1915, Zelinsky, on the basis of laboratory and pilot-plant experiments, pointed out, for the first time in the history of petroleum science, the effectiveness of aluminosilicates and oxide catalysts in the cracking of hydrocarbons.

During the first world war Zelinsky extended his investigations on the catalytic cracking and pyrolysis of petroleum distillates, and he helped in the creation of a Russian toluene industry. Guided by his theoretical concepts and experimental investigations and moved by feelings of deep patriotism and love of the Fatherland, N. D. Zelinsky, at the height of the first world war, invented the first universal charcoal gas mask in the world; it saved the lives of hundreds of thousands of Russian soldiers on the battlefield.

In the spring of 1915, as soon as the news arrived of the despicable use by the Kaiser's armies of poison gas against the French, and later the Russian, armies, Zelinsky temporarily abandoned all his other investigations and, with his characteristic energy and zeal, set about developing a reliable means of protection. The idea of using active charcoal for the absorption of poisonous substances (chlorine, phosgene, mustard gas, etc.) arose as the result of his thorough experimental investigations on the absorption of gases and vapors by highly porous substances.

After thorough trials on himself personally, with the participation of his faithful laboratory assistant S. S. Stepanov (who worked hand in hand with him for a total of fifty years), and after the delays that were inevitable at that time in Prince Oldenburg's department, Zelinsky's gas absorber fitted to a rubber mask designed by the engineer Kumant received the warm approval of the High Command, and was adopted in February 1916 for the equipment of the Russian Army.

In his work on the devising of the gas mask, Zelinsky received valuable help not only from Stepanov and Kumant, but also from his colleague Prof. V. S. Sadikov. With justifiable pride, in discussing the gas mask, Zelinsky said, "I invented it not for attack, but for the protection of young lives from suffering and death".

In 1917, shortly after the overthrow of the autocracy, Zelinsky found it possible to return to his chair in Moscow University. After the victory of the Great October Socialist Revolution, Zelinsky's second Moscow period of scientific teaching, and social activitiesbegan, and it continued to the end of his long, full, exemplary life. This brilliant period, which lasted more than one-third of a century, was the most fruitful of all —so full of brilliant investigations that it is quite impossible to treat them in a short memorial sketch.

The Communist Party of the Soviet Union and the Soviet government, with the scientific giants Lenin and Stalin at their head, have created all the necessary conditions for the blossoming forth of true science, having paid special attention to the requirements of scientific workers. And under these conditions the remarkable talent of N. D. Zelinsky has developed in its full strength in unison with the varied manifestations of the majestic creative forces of the highly gifted Russian people, which are directed toward the creation of a bright future for the whole of humanity.

Having resumed his scientific and teaching activities at Moscow State University with particular vigor, N. D. Zelinsky did not interrupt them even at the most difficult periods of the civil war and Anglo-American intervention. Along with him, in the cold half-illuminated laboratories, his faithful assistant S. S. Stepanov and the first students of his second Moscow period, B. A. Kazansky and B. V. Maksorov, worked unselfishly, and they were soon joined by a new group of students of the revivified Moscow State University, including among many others, A. N. Nesmeyanov, K. A. Kocheshkov, M. I. Ushakov, and G. S. Pavlov.

When the interventionists seized the Caucasian oil fields and Soviet aviation was deprived of gasoline supplies, Zelinsky, on the basis of his researches on the cracking of hydrocarbons in presence of aluminum chloride, proposed, and quickly realized in practice, a new method of manufacturing gasoline from the large stocks of petroleum residues and solar oil that were then to be found in the central provinces. This method for the manufacture of aviation fuel rendered extremely valuable service to the young heroic Red Army. Again N. D. Zelinsky showed himself to be a fervent patriot of his now already socialist Fatherland. Shortly after this, by his work on the pyrolytic preparation of benzene from petroleum, Zelinsky made a valuable contribution to the synthetic dye industry that was then coming into being in our country.

It is natural that Zelinsky first of all resumed his long-standing investigations on the catalytic transformations of hydrocarbons and on petroleum chemistry, developing these in close association with his further work on the synthesis of more complex cycloalkanes. In addition to difficultly accessible monocyclic hydrocarbons, Zelinsky synthesized and carefully characterized many interesting bi- and tri- cyclic substances, and also condensed systems.

Zelinsky continued to devote much attention to the synthesis and heterogeneous - catalysis reactions of little known hydrocarbons having spiran structures, which are very interesting from the stereochemical point of view. Together with N. I. Shuikin and N. V. Elagina, he synthesized a number of spiroalkanes and made a detailed study of their properties and reactions under various conditions. Together with A. E. Uspensky, K. A. Kocheshkov, M. I. Ushakov, B. A. Kazansky, and A. F. Plate, he synthesized difficultly accessible bridged bicyclic systems.

With great persistence and thoroughness, Zelinsky, with the aid of numerous students and coworkers, investigated the chemical nature and composition of gasoline distillates from the petroleums of almost all the important oil fields of the USSR, particularly the Caucasian fields. By detailed and careful work he determined the nature of the various heterogeneous - catalysis reactions of the cyclic hydrocarbons occurring in the gasoline - ligroin fractions, developed new methods for the catalytic treatment of petroleum, and obtained new material in confirmation of the theory of the organic origin of petroleum.

In their work on the catalytic dehydrogenation of gasoline fractions, N. D. Zelinsky and N. I. Shuikin already in 1932 made the extremely important observation that aromatic hydrocarbons are formed in presence of a nickelized alumina catalyst at somewhat above 300° not only as a result of the smooth dehydrogenation of cyclohexanes, but also at the expense of hydrocarbons of other classes. Together with B. A. Kazansky and A. F. Plate in 1934, Zelinsky discovered the very interesting reaction of the opening of a five-membered cycle by means of hydrogen in presence of platinized charcoal at 300—310°, i.e. the hydrogenolysis of a five-membered alicyclic system in which there was practically no strain.

In the same year N. D. Zelinsky and N. I. Shuikin showed experimentally for the first time the existence of free methylene radicals under the conditions of methane elimination from cyclohexane in contact with a nickelized alumina catalyst at 330—350°. It was thus shown that free radicals can arise by the breakdown of an organic substance in presence of a highly active catalyst, even at such comparatively low temperatures as 300—350°.

Together with a team of students and coworkers, Zelinsky has developed, and introduced into industrial practice, an original method for the preparation of toluene and high-quality aviation fuels from petroleum on the basis of further improvements in the dehydrogenational - catalysis method that he discovered. In the course of the development of this new Soviet process, the scientific principles on which the theory and practice of the use of highly active and stable metal catalysts of the platinum group are based have been greatly extended. All that has been recently brought into wide use in the U.S.A. under the name of the platforming process, which has been loudly proclaimed as the achievement of American scientists (V. Haensel and others), was begun and completed in the traditional investigations of N. D. Zelinsky and his school.

Several years before the first "sensational" American publications in 1949, this process, under the name of "GRB" (the initials of words meaning "deep reforming of gasolines"), was developed by N. D. Zelinsky's students in the Institute of Organic Chemistry of the USSR Academy of Sciences, use being made of alumina and aluminosilicate catalysts containing small amounts of platinum, and also of oxide catalysts containing palladium and nickel.

As he attached great importance to the use of modern physical methods by research chemists, N. D. Zelinsky, together with Academicians B. A. Kazansky and G. S. Landsberg, introduced the combination light-scattering method (i.e., Raman method —Publisher) for the detailed investigation of gasolines, and this, in conjunction with dehydrogenational-catalysis, chromatographic adsorption, and precise rectification, gave valuable scientific and practical results in the quantitative analysis of hydrocarbon mixtures.

We cannot leave the excellent investigations of N. D. Zelinsky on hydrogenational-catalysis without mention; he developed methods for the vapor-phase hydrogenation under normal pressure not only of ethylenic bonds, but also of the more stable bonds in benzene, pyridine, and pyrrole nuclei. He used finely dispersed palladium and platinum deposited on active charcoal or asbestos, and so proved the incorrectness of P. Sabatier's assertion that platinum and palladium are unsuitable for hydrogenations in a continuous-flow system. Zelinsky discovered still another catalyst of the platinum group having notable hydrogenation properties, namely osmium; he was the first to effect, with the aid of finely dispersed osmium, the delicate reaction of the smooth hydrogenation of the furan nucleus. He carried out the vapor-phase hydrogenation of 2-methylfuran (sylvan) to tetrahydro-2-methylfuran, a reaction that served as the starting point for the development of an accessible method for the synthesis of numerous γ-oxides.

Exceptional interest is presented by the fundamental investigations of Zelinsky and his students on the chemistry of proteins and of their component amino acids. His first investigation as a student was already directly related to this field.

In these investigations Zelinsky developed a new simplified method for the synthesis of α-amino acids by the action of an aqueous solution of ammonium chloride and potassium cyanide on aldehydes and ketones. By this cyanhydrin method a whole series of complex hydroxy-amino acids were obtained, and their role in the building of protein molecules constantly engaged Zelinsky's attention. His cyanhydrin method is now a classical one for the synthesis of α-amino acids, and it has passed in this form into textbooks and handbooks throughout the world.

The problem of the structure of proteins has been the subject of close attention for more than a century.

The remarkable investigations of N. D. Zelinsky and his talented teams of students and coworkers, among whom we may make particular mention of V. S. Sadikov, N. I. Gavrilov, N. A. Shlezinger, E. F. Dengin, I. V. Kulikov, A. I. Annenkov, A. B. Silaev, M. A. Prokofyev, and M. M. Botvinnik, have made an exceptionally valuable contribution to the study of protein structure. Zelinsky approached this field for the first time with the criteria and procedures afforded by new methods of synthesis and catalysis, and by his investigations he brought about a real revolution. By the application of his original method of high-pressure hydrolysis to the study of protein molecules, he showed that in most cases the primary hydrolysis products of proteins formed in presence of dilute acids and alkalis as catalysts were heterocyclic compounds, piperazinediones.

On the basis of his investigations over many years (they were begun in St. Petersburg in 1912) on high-pressure hydrolysis, Zelinsky, in conjunction with V. S. Sadikov, worked out a theory of the cyclic structure of protein molecules. In subsequent investigations with N. I. Gavrilov and others, he unified his piperazinedione theory with E. Fischer's polypeptide theory, and so solved one of the most difficult problems concerning the fundamental microstructure of protein.

The research activities of N. D. Zelinsky form a brilliant example of innovation in science; he possessed in the highest degree that feeling for the new which is the powerful prime mover in progress. Foreseeing the great importance that radioactive radiations would have in scientific investigation and in practical applications of the highest importance to the state, Zelinsky, already in 1922, studied the effects of radium radiation on cyclohexene. The results of this work were communicated by Zelinsky to the third Mendeleev Congress on Pure and Applied Chemistry under the title "Decomposition of Hydrocarbons by the Energy of Radiation from Radium".

Zelinsky was a pioneer in the USSR in the study of various reactions at very high pressures (higher than 1000 – 2000 atm), and in 1939 he, together with L. F. Vereshchagin, established the Super-high Pressure Laboratory in the Institute of Organic Chemistry of the USSR Academy of Sciences. At the present time the reactions of a great variety of organic substances are being studied in this laboratory over a wide range of pressures (3000 – 50,000 atm).

In a short memorial sketch it is impossible to discuss, even schematically, the results of the extensive and important investigations of N. D. Zelinsky. We should like to discuss his original work on the origin of petroleum, his remarkable investigations with Ya. T. Eidus on the catalytic synthesis of artificial liquid fuel from carbon monoxide and hydrogen, his promising researches on the catalytic condensation of acetylene to aromatic hydrocarbons, and the extremely interesting, though for some reason not very well-known, work on the synthesis of naphthenic acids and the study of their chemical nature. It would be desirable to describe Zelinsky's investigations over many years on the conditions for the synthesis of ketones of the cyclohexane and cyclopentane series (reactions formally analogous to the Friedel – Crafts reaction in the aromatic series), which were carried out by him in conjunction with E. S. Przhevalsky, S. S. Nametkin, I. F. Gutt, B. M. Berkengeim, and, particularly, E. M. Tarasova. One would have to describe Zelinsky's investigations on the catalytic synthesis of chloroprene, work on the catalytic desulfurization of petroleum and shale distillates, on the chemical nature of distillates from sapropelite tar, on the deparaffination of petroleum, on the gasolinization of petroleum, on the development of interesting syntheses of dimethylindigo, of phenol from chlorobenzene, acetone from acetylene, and phthalic anhydride by the catalytic oxidation of naphthalene.

It would be important to note also Zelinsky's investigations on the chemistry of hormones of the androsterone group (with M. I. Ushakov), the remarkable syntheses of branched carboxylic acids of the aliphatic – alicyclic series having an antitubercular bacteriostatic effect (with L. S. Bondar), and his new method for determining fats in an animal organism.

We must refer also to Zelinsky's investigations in biochemistry: his remarkable work on the elucidation of the causes of hydrogen sulfide fermentation in deep zones of the Black Sea, which is associated with the leading part that he played in the 1891 expedition on the gunboat "Zaporozhets"; his investigations on the chemical nature of the organizer responsible for the growth of secondary limbs on the axolotl; and other very interesting investigations in this attractive field.

The list of N. D. Zelinsky's important investigations could be continued further without any particular difficulty.

These extensive contributions to science, the whole of this great scientific feat, N. D. Zelinsky performed in close association and collaboration with his numerous students and collaborators, whom he painstakingly trained in the best traditions of foremost Russian science.

In the course of his purposeful scientific research work N. D. Zelinsky created the greatest school of organic chemistry in our country.

Up to the very last days of his life N. D. Zelinsky was closely associated with his students: Academicians A. N. Nesmeyanov, B. A. Kazansky, A. A. Balandin, Corr. -member K. A. Kocheshkov, Doctors of Chemical Sciences Yu. A. Arbuzov, P. P. Borisov, B. M. Berkengeim, N. I. Gavrilov, G. D. Galpern, Ya. I. Denisenko, K. P. Lavrovsky, R. Ya, Levina, Yu. G. Mamedaliev, S. S. Novikov, G. S. Pavlov, A. F. Plate, S. R. Sergienko, M. B. Turova-Polyak, N. I. Shuikin, Ya. T. Eidus, Yu. K. Yuryev, Doctor of Physicomathematical Sciences L. F. Vereshchagin, Candidates of Chemical Sciences L. S. Bondar, M. M. Botvinnik, G. R. Gasan-Zade, N. V. Elagina, P. G. Ivanov, E. I. Margolis, G. M. Marukyan, D. A. Morozova, I. A. Musaev, N. A. Poddubnaya, M. A. Prokofyev, S. E. Rank, A. B. Silaev, E. M. Tarasova, A. N. Titova, I. I. Tits-Skvortsova, S. I. Khromov, E. P. Tsintsevich, E. M. Shankhazarova, M. V. Yushkevich-Gaverdovskaya, M. S. Eventova, and many others. The list of students and coworkers with which N. D. Zelinsky has published scientific papers contains more than 150 people.

Apart from his students and coworkers, Zelinsky always had many friends and admirers among eminent men of science and art.

Zelinsky was always a convinced supporter of well-harmonized team work in scientific work. Already in 1922 in his concluding address at the close of the third Mendeleev Congress he said: " The most important and fundamental problems with respect to our concepts of nature require joint investigations for their solution; mathematicians , engineers, physicists, chemists, biologists, bacteriologists, medical men, mineralogists, geologists, and even astronomers must take part, for the microcosm of chemical molecules and the structure of atoms are bound to reflect in themselves elements of the structure of the universe".

In the Soviet Union it would be difficult to find a higher chemical teaching establishment, a research institute, or a large chemical plant in which no student of Academician Zelinsky or of his students or coworkers was to be found.

As a true patriot of his great Fatherland, N. D. Zelinsky always carried out much responsible social work. It may be said without exaggeration that in the ranks of the older generation of scientists Zelinsky was one of the most eminent social workers, carrying on the best traditions of our progressive Russian intelligentsia.

Already under the reactionary political conditions of the Tsarist regime, N. D. Zelinsky was a progressive university worker. As an advocate of higher education for women, he organized at the end of the nineties an organic chemistry department in connection with the higher courses for women that were then starting in Moscow, and he was the first director of the department. He took an active part in the organization of the Shanyavsky People's University in Moscow.

From 1893 onward, N. D. Zelinsky took an active part in the work of the Moscow Society of Investigators of Nature, the oldest such society in the country, and from 1935 to the end of his life he was president of this society. In 1921 he was elected an honorary member of this society.

From the nineties of the last century onward Zelinsky joined in the activities of the Society of Amateurs in Natural Science, Anthropology, and Ethnography, the Kh. S. Ledentsov Society for the Encouragement of Progress in Experimental Science and its Practical Application, and particularly the Russian Physicochemical Society. From 1934 until his death he took a leading part in the D. I. Mendeleev All-Union Chemical Society, which is the successor to the Russian Physicochemical Society. Here also Zelinsky rightly earned the title of honorary member of the Society.

Even in his declining years, N. D. Zelinsky did not discontinue his scientific, teaching and social work. A fervent patriot of our great Fatherland, he responded quicklyand directly to all the social and political events of our time, actively participating in the struggle of progressive humanity for peace. As early as August, 1950, he wrote in the journal "Technology for Young People": "I wish to add my voice to those of hundreds of millions of honorable people on our planet who understand that it is not sufficient simply to wish for peace, and that it is necessary actively and passionately to struggle for peace and tranquillity on the earth". He wrote further: "We scientists cannot remain to one side and watch in indifference how the barbarians of the twentieth century are preparing to set a new worldwide conflagration going and to strew the cities of the world with atom and other bombs in order to achieve their mad and fantastic purpose of world domination".

N. D. Zelinsky was an exemplary man and citizen, who provided an example of the very highest, truly socialist productivity of labor, worthy of imitation in every way. Throughout the whole of his long life he confidently moved on toward the summits of his favorite science, and to the end he devoted his science to the service of his great people and to the general task of constructing a communist society.

Together with the chemical society of our flourishing Fatherland we bow with feelings of the deepest respect in memory of the eminent Soviet chemist Academician Nikolai Dmitrievich Zelinsky.

A. N. Nesmeyanov
A. V. Topchiev
B. A. Kazansky
N. I. Shuikin

A. M. BUTLEROV

(in celebration of the 125th anniversary of his birth)

September 6, 1953, saw the completion of 125 years since the birth of the great Russian chemist, Aleksandr Mikhailovich Butlerov, one of the founders of modern organic chemistry and author of the theory of the chemical structure of organic compounds, which for more than ninety years has served, and still continues to serve, as the basis of all theoretical and experimental investigations in organic chemistry.

A. M. Butlerov was born on August 25 (September 6, New Style), 1828, in Chistopol in the province of Kazan, and he spent his childhood on his father's estate. In 1844 he left the First Kazan Gymnasium and began to attend lectures at the Department of Physics and Mathematics of the Faculty of Philosophy at Kazan University. He was not accepted as a student of the university until the next year, when he attained the age of seventeen. At the university Butlerov took a great interest in the natural sciences biology and chemistry. His interest in biology was reflected in his choice of subject for his candidate's thesis: "Butterflies of the Volga — Ural Fauna". His interest in chemistry developed in his student years while working in the chemical laboratory under Professors N. N. Zunin and K. K. Klaus. On completing his course at the university, Butlerov, at the request of the university council, gave courses in chemistry, physics, and physical geography to students of various faculties.

In 1851 Butlerov defended his Master's thesis on the theme "The Oxidation of Organic Compounds", and in 1854 he defended his Doctor's thesis, which was entitled "Ester Oils". On September 25 he was elected by the council as extraordinary professor of chemistry, and from that time until 1869, when he went to St. Petersburg, his scientific and teaching activities were associated with Kazan University.

Butlerov's theses are of the nature of reviews or compilations, and he did not publish them. His first experimental investigations, which were not unified by any common concept, were published during 1852 — 1857, and his first public discussion of a theoretical question occurred at Paris in 1858, when he read a paper, which has not been published, to the Paris Chemical Society on the constitution of substances. Some of the material contained in this paper was incorporated in Butlerov's article entitled "Observations on A. S. Couper's New Chemical Theory". In this article he develops ideas concerning carbon ("mechanical") types or "types of molecular structure", and he points out that "the time has come for us to go further than Gerhardt".

While abroad in 1857 — 1858, Butlerov began a series of investigations on methylene derivatives, which were continued further over a number of years at Kazan and St. Petersburg. He prepared methyleneiodide (and later, the bromide and chloride), and from this the diacetic ester of methylene glycol, which, however, did not give methylene glycol itself when hydrolyzed. An attempt to prepare the oxalic ester led to the isolation of a polymer of formaldehyde, which Butlerov called "dioxymethylene". By the action of ammonia on this substance, hexamethylenetetramine was prepared for the first time, and by the action of lime water a sugarlike substance "methylenitan". In this way the first laboratory synthesis of a carbohydrate was performed. The attempts made in the course of these investigations to isolate methylene in the free state were not successful: ethylene and its homologs were always formed.

In 1858, A. M. Butlerov was elected as an ordinary professor of Kazan University, and at the beginning of 1860 he was appointed rector. He occupied this post for three years, and it was with great difficulty that he managed to free himself from his heavy administrative duties.

In 1861 Butlerov set off on his second foreign mission, and at the Thirty-sixth Congress of German Physicians and Naturalists he read a paper on "The Chemical Structure of Substances", in which he stated the basic principles of the theory of structure.

In the fifties and early sixties of the last century, chemistry found itself, as Butlerov expressed it, "in an awkward situation", because the chemical theory then in existence could not satisfactorily interpret and unify the huge quantity of facts that had accumulated. Gerhardt's theory of types no longer satisfied chemists, because it was unable to explain a large number of addition reactions that had become known at that time and it permitted a large number of rational formulas for a given substance indicating the directions in which the substance must decompose when entering into various metathetic reactions. Also, most chemists acknowledged the concept of "constitution" of chemical compounds, which they understood, following Gerhardt, as the "true arrangement of the atoms in the molecule". For the determination, however, of this "true", i.e. spatial, arrangement of the atoms, the necessary means of investigation did not exist in the chemistry of that time, and for this reason many regarded such a problem as insoluble in principle. This had become the source of doubts in the possibility of formingsound theoretical views in chemistry, and of a tendency to agnosticism and return to empirical formulas. Kekulé wrote in the first volume of his textbook: "In chemistry we cannot even speak of true theory: all so-called theoretical considerations are based on probability and expediency." In 1861 he announced that he would give up the use of type formulas and use only empirical formulas in organic chemistry.

In his paper, A. M. Butlerov first criticized the type concepts and then spoke in favor of the hypothesis that atomicity (valency), a definite and unchangeable property of elements, could serve as a basis for the creation of a general theory of chemistry. In order to avoid superfluous hypothetical concepts, he proposed to set aside the hypothetical (at that time) "physical" atoms ("ultimate indivisible particles of elements") and operate with chemical atoms, by which he understood the smallest amount of an element that could enter into the composition of the molecule of a complex substance. Contrasting the mechanical arranging of atoms in a molecule with the concept of chemical structure, A. M. Butlerov defined the latter as follows in his paper: "On the basis of the concept that every chemical atom entering into the composition of a body takes part in the formation of the latter, acting there with a definite amount of the chemical force affinity that belongs to it, I define chemical structure as the distribution of the action of this force, as a result of which chemical atoms that directly or indirectly influence one another are united in a chemical particle.

"The well known rule that the nature of a complex particle is determined by the nature, amount and distribution of the elementary components, may be changed, I consider, as follows: The chemical nature of a complex particle is determined by the nature of the elementary component parts, their amount, and the chemical structure." Later, speaking about chemical structure, Butlerov expressed himself more briefly and definitely, defining it as "the distribution of chemical bonds existing between atoms in a particle".

In the fundamental theses of the Butlerov paper, therefore, the concepts of atomicity (valency) of the elements, of the bonds between atoms in a complex molecule, and of the dependence of the properties of a complex substance on its chemical structure were brought together and unified. This made it possible to place chemical theory on sound ground and to link it directly with chemical experiment. If, in fact, the properties of a complex substance are determined by its structure, then we may form an opinion of its structure from its chemical reactions, and knowing the structure of a substance, we may predict its properties. In his paper, A. M. Butlerov points out that reactions of all kinds (addition, decomposition, and metathesis) can be used for the determination of chemical structure, and he advances a number of empirical rules that may be used for this purpose. Without considering what concrete form must be taken for the outward expression of structural formulas, Butlerov advanced the view that only one structural formula was possible for each substance and that in the future, when the laws relating properties to structure became known, such a formula would express all the properties of the given substance. In his paper Butlerov raised, for the first time, the question of the mutual effects between atoms present in the same molecule, but not directly united, indicating that the views that he had advanced would help to provide an answer to this question in the future.

The work carried out by Butlerov in the years that followed had the object of developing the fundamental concepts of the theory of chemical structure and rendering them more precise. He considered, for example, questions concerning the differences in the nature of the valencies of carbon, nitrogen, and sulfur atoms, and he finally came to the conclusion that the hypothesis that the units of valency were different in nature was not correct. He studied also the reaction of phosgene with dimethylzinc, thus hoping to effect the direct synthesis of acetyl chloride or acetone, as the theory of chemical structure predicted; apart from substances containing the acetyl group, the main product of this reaction was found to be a crystalline compound that behaved like an alcohol, later shown to be tert-butyl alcohol.

An extremely important contribution to the development of the theory of chemical structure was Butlerov's fundamental work on "Various Explanations of Certain Cases of Isomerism". In this he shows, very clearly and convincingly, that the phenomenon of the isomerism of organic compounds is to be explained by difference in structure associated with identity in composition and molecular size, the differences in properties being, therefore, explained by differences in the mutual effects of atoms in the molecule; this is confirmed by numerous examples.

This paper must be associated with another large theoretical article "The Systematic Application of the Principle of Atomicity to the Prediction of Cases of Isomerism and Metamerism", in which he shows that from the point of view of the theory of structure the prediction of the existence of isomers is only a matter of the construction of diagrams; he predicts the isomerism of saturated hydrocarbons and the existence, in particular, of isobutane.

It was at this period (1864) that Butlerov was working on a textbook of organic chemistry based on the theory of structure. In 1864—1866 the first edition of "Introduction to the Complete Study of Organic Chemistry" appeared in Kazan, and this gave a new systematic treatment of organic compounds, extensively discussed the whole of the factual material available in the light of the theory of chemical structure, and developed its fundamental concepts, particularly that of the mutual effects of atoms in the molecule. In 1867—1868 the "Introduction" was issued in a German translation, and this edition helped greatly to spread the concepts of the theory of chemical structure beyond the frontiers of Russia.

At the same time, Butlerov's experimental work continued. A series of investigations was devoted to tert-butyl alcohol and tertiary alchols in general. Tert-butyl alcohol was prepared by Butlerov by the action of dimethylzinc on acetyl chloride; its properties were finally established, and various derivatives were synthesized, for example, the acetic ester and tert-butyl iodide; isobutane and isobutene were prepared, the synthesis of the former being particularly important, since it confirmed Butlerov's prediction of the existence of isomerism among saturated hydrocarbons, and the actual nature of this isomerism was explained from the point of view of the theory of structure; with isobutene (2-methylpropene) the reaction of polymerization was observed for the first time. To this same period (1867) belongs work on the synthesis of alcohols from 2-iodoethanol and dialkylzincs; the unexpected formation of secondary alcohols, instead of the primary alcohols predicted by the theory of structure, led Butlerov to the conclusion that during this reaction there occurs an intramolecular rearrangement, which is also explicable from the point of view of the theory of structure.

A large number of new experimental facts, established not only by Butlerov, but also by other chemists in Russia and abroad, strengthened the foundation of the theory of chemical structure and helped it to become more and more widely known. With increasing frequency, however, cases occurred in which the name of A. M. Butlerov was ignored in publications concerned with matters relating in one way or another to the theory of structure. While remarking on the large number of examples that had appeared which confirmed the correctness of his theoretical views, Butlerov pointed out that "all this, however, does not prevent many foreign chemists from making insufficient acknowledgement of the part that I played in the development of the views that are now coming to be accepted in chemistry, and from frequently announcing as a new idea that which I have already announced". This position prompted him to go on a third mission abroad in 1868 in the hope of defending his priority by personal exchange of views with foreign chemists. This object, however, was not attained, and in foreign chemical literature the theory of structure is more often associated with the names of Kekulé and Couper, than with that of A. M. Butlerov.

While he was abroad, Butlerov was elected to the chair of chemistry at St. Petersburg, and he began to lecture there on organic chemistry in January, 1869. In March, 1870, he was elected as an Adjunct of the Academy of Science; in December, 1871, he was elected as an Extraordinary Academician, and in January, 1874, as Ordinary Academician in Chemistry. The St. Petersburg period of his life was mainly devoted to activities in these two institutions, the Academy of Sciences and St. Petersburg University.

Butlerov's scientific work in the St. Petersburg period developed in the following directions. First of all, he made a closer examination of the methylene derivatives that he had already investigated and showed that in the vapor state "dioxymethylene" was the monomer "oxymethylene" (formaldehyde, CH_2O), whereas in the solid state it was the trimer "trioxymethylene", of cyclic structure; he showed, also, that with ammonia gaseous formaldehyde forms the same hexamethylenetetramine as polyoxymethylene does.

A series of investigations followed that formed a continuation of those already begun at Kazan; they concerned tert-butyl alcohol, 1,1-dimethylpropionic acid, and other compounds that could be prepared from tert-butyl alcohol. It was shown that this alcohol could be readily prepared from isobutene by direct hydration in presence of sulfuric acid; it was also possible to prepare ethyl alcohol from ethylene, though under more severe conditions. Having obtained tert-butyl alcohol in large amounts and in a pure condition, Butlerov studied its oxidation with chromic acid mixture (acetic acid, acetone, and isobutyric acid are formed) and prepared, via the iodide and nitrile, a new isomer of valeric acid, 1,1-dimethylpropionic acid. From the acid chloride of this and dimethylzinc he synthesized pinacolone; he established the structure of this substance and so made a correct interpretation of the mechanism of the pinacolone rearrangement possible.

Continuing his investigations of isobutene and its reactions, Butlerov considered the question of the structure of unsaturated compounds and advanced the view that they contained multiple bonds, in support of which he provided convincing experimental evidence. He continued experiments on the polymerization of isobutene and other olefins in presence of sulfuric acid and boron trifluoride, and discussed the mechanism of the polymerization and the structure of the polymers. The results obtained by Butlerov in this field were much in advance of the contemporary organic chemistry, and only very much later were they placed at the basis of technical processes for the synthesis of high-quality components of motor fuels. In one of the investigations, devoted to "diisobutylene", the concept of the tautomerism of organic compounds is developed; its treatment as reversible equilibrium isomerization is fully in accord with modern views on this phenomenon.

Butlerov's experimental investigations in the last period of his life stand somewhat apart from the previous ones. They concern some experiments with quinine and cinchonine, which helped in the elucidation of the structures of these alkaloids, and also a description of asarone, obtained from the plant Asarum europeum, and a study of its structure. A quite special position is occupied by his "Note on Atomic Weights" (1882), in which Butlerov discusses the question of the possibility of the atomic weight of an element varying according to the external conditions. He suggested that Prout's hypothesis, according to which the atomic weights of the elements are expressed by whole numbers with respect to hydrogen, may be true under conditions that have still to be defined, and that the usually observed departures of atomic weights from whole numbers result from nonobservance of these conditions. Experiments were begun with the object of finding these conditions and hence of experimentally confirming the complex character of atoms, but Butlerov did not succeed in completing them.

The two last theoretical papers of A. M. Butlerov are concerned with the theory of chemical structure. Toward the beginning of the eighties of the last century this theory occupied a leading position in organic chemistry, in which an enormous number of facts had accumulated which confirmed it and helped to develop it. Voices were still sometimes raised however — and they belonged to some of the most eminent chemists (Kolbe, Bertelot, Menshutkin) — expressing doubt in its correctness and fruitfulness. In his paper "Present Significance of the Theory of Chemical Structure" (1879), Butlerov showed in an exceptionally convincing manner that the theory was soundly based on an enormous amount of experimental material and had an extraordinary ability to predict. He countered objections made to the static character of structural formulas, pointing out that "we now regard chemical structure not as something dead and immobile; we consider, on the contrary, that it is endowed with constant movement, which is contained in its smallest particles, the individual relationships between which are undergoing continual changes, which integrate to a certain constant average result". He objected also to the idea that the theory of chemical structure was associated with the idea of the constant valency of elements, and he remarked that the theory was undeservedly condemned as denying the existence of mutual effect of atoms present in the same molecule, but not directly united.

In the second paper "Chemical Structure and the 'Theory of Substitution' ", Butlerov attacked the idealistic basis of the theory of substitution and, comparing it with the theory of structure, concluded that its predictions were correct only when the chemical structures, of the compounds under examination were already established. After these papers objections to the theory of structure ceased entirely, and it received general acknowledgement; it has maintained its leading role right up to the present day.

Throughout his whole life A. M. Butlerov combined his scientific activities with public and social activities. He was one of the leading members of the Russian Physicochemical Society from the time of its foundation, he took an active part in the congresses of Russian naturalists and physicians, gave public lectures to wide audiences, was one of the organizers of the higher courses for women, and was an active member of the Free Economic Society, in which he worked very vigorously on the development of rational apiculture in Russia.

In discussing Butlerov's public activities we cannot omit a reference to his articles directed against the then-dominant "German party" in the Academy of Sciences — a party of academicians of non-Russian origin, who were trying to exclude the great Russian scientists from membership of the Academy. As an example of their reactionary activities we may refer to the nonelection of D. I. Mendeleev at the Academy elections of 1882, which prompted an exceptionally vehement protest from Butlerov in the article "Russian, or merely Imperial Academy of Sciences?", which was published in the newspaper "Russia".

On August 5 (17, New Style), 1886, A. M. Butlerov died suddenly, at the height of his creative activities. His role in the development of Russian and world chemical science cannot be overestimated. His name stands with those of Lomonosov and Mendeleev, and is an object of pride for our people.

THERMODYNAMIC STABILITY OF VARIOUS STRUCTURES IN BINARY INORGANIC CRYSTALS

Yu. M. Golutvin

The question of the relative stabilities of various structures for simple binary inorganic compounds in the solid state is a very complex one. A study of this question shows that the problem of the thermodynamic stabilities of the crystalline phases referred to above may be solved by the use of the quantity ρ, the ratio of the univalent and crystal radii of an ion, which has been introduced into thermodynamic investigations by the author and Kapustinsky [1]. Their treatment permitted a quantitative relation to be found between heats of formation per gram equivalent $\frac{\Delta H^{\circ}}{W}$) and the values of ρ for the cation and anion. It was found that, for a series of compounds having a common cation or anion, $\sqrt{\frac{-\Delta H^{\circ}}{W}}$ increased, when comparisons were made along the groups and periods of Mendeleev's system.

When a compound is found, within the series under comparison, for which $(\rho_{cat} - \rho_{an}) = 0$, it has a maximum heat of formation per gram-equivalent ("inversion point"): on each side of this point $\sqrt{\frac{-\Delta H^{\circ}}{W}}$ for the other compounds fall on straight lines sloping downward. The general form of the graph for a series of compounds having a common anion and showing a point of inversion is given in Fig. 1 [the case of a comparison in a period in which the maximum range of variation of $(\rho_{cat} - \rho_{an})$ occurs]. The value of ρ expresses the effect of Coulomb forces on the dimensions of an ion of constant electronic configuration [2], and it characterizes the relationship between the attractive and repulsive forces that the given ion exhibits with respect to the other ions in the crystal lattice.

The greater the value of ρ for a given ion, the greater, evidently, will be its ability to attract oppositely charged ions, and the less will be its ability to repel the electron atmospheres of these ions. In this connection, the ρ-values may be regarded as the polarizabilities of the ions.

The fact that, in a series of compounds under comparison, the compound for which $\rho_{cat} = \rho_{an}$ has the maximum heat of formation per bond shows that in this particular case the strongest bonds are formed, these, apparently, being of a predominantly ionic character. For compounds in which ρ_{cat} and ρ_{an} are not equal, the heat of formation per bond is less, indicating the increased "diffuseness" and lower ionic character of the bonds.

It follows from this that the difference $(\rho_{cat} - \rho_{an})$ may be regarded as a measure of the one sided polarization of ions in the crystal lattice. Hence, if the cation and anion have nearly equal ρ values, such compounds must have bonds that are essentially of the ionic type, because polarization phenomena cannot occur here to an appreciable extent. On the other hand, if ρ_{cat} and ρ_{an} are appreciably different in value, then, owing to the preferential polarization of one of the ions, the bonds must depart from the ionic type. If $\rho_{an} > \rho_{cat}$ [i.e $\rho_{cat} - \rho_{an}) < 0$], the cation will be polarized by the anion (see, for example, the distribution of electron density in Mg_2Si crystals, studied by Ageev and Guseva [3]. Owing to the lower deformability of cations, as compared with anions, the bonds must nevertheless preserve a still appreciable measure of ionic character.

When there is a considerable predominance of ρ_{an} over ρ_{cat}, we may expect the formation of structures of the CaC_2 type, in which polarization is reduced owing to the formation of voluminous multiple anions having a lower polarizability than simple anions. If $\rho_{cat} > \rho_{an}$ (i.e. $(\rho_{cat} - \rho_{an}) < 0$), the anions will be polarized by the cations to an extent that may be considerable, owing to the greater deformability of the anions, and this should lead to the formation of covalent structures; this includes also the case of compounds containing multiple cations (ρ_{cat} very much greater than ρ_{an}). These conclusions are confirmed by the experimental facts. Comparison of the data in the literature on the structures of the main classes of binary inorganic compounds and the types of chemical bonds that they contain [4, 5, 6, 7, 8] with the values of $(\rho_{cat} - \rho_{an})$ leads to the results given in Tables 1 and 2. Data for the calculation of ρ for certain other ions may be found in a paper by Kordes [9].

Table 2 does not include compounds of elements giving ions having 18-electron outer shells. Compounds of elements of this type will be examined separately.

Mapping of the electron density between the atoms provides the most reliable criterion for the determination of the type of chemical bond in the crystals. At present, however, very few such data are available for inorganic systems, and in the majority of cases it is necessary to deduce what type of bond is present in a particular crystal from indirect data (electrical conductivity, tendency to undergo electrolytic dissociation in polar solvents and in the melt, the type of crystal lattice, the interatomic distances, the angles between the bonds, melting and boiling points, tendency to undergo hydrolysis, mechanical properties, color, etc.). Owing to these circumstances and the presence of bonds of intermediate character, the assessment of types of bonds in various compounds, as given in Table 2, must be regarded as approximate and as expressing only the basic tendency that is characteristic of the particular compound.

The first row of Table 2 contains compounds having chemical bonds that we have described as covalent-ionic. These include structures having weak cation-anion bonds of appreciable ionic character and containing multiple anions having considerably stronger covalent anion-anion bonds. Such structures are most stable for compounds characterized by large negative values of $(\rho_{cat} - \rho_{an})$.

TABLE 1

Values of ρ for Various Ions

Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ
Cations													
Li^{+1}	1.190	Be^{+2}	1.42	B^{+3}	1.75	C^{+4}	1.93	N^{+5}	2.27	O^{+6}	2.44	F^{+7}	2.72
Na^{+1}	1.184	Mg^{+2}	1.26	Al^{+3}	1.44	Si^{+4}	1.59	P^{+5}	1.74	S^{+6}	1.83	Cl^{+7}	1.88
K^{+1}	1.143	Ca^{+2}	1.19	Sc^{+3}	1.31	Ti^{+4}	1.41	V^{+5}	1.49	Cr^{+6}	1.56	Mn^{+7}	1.63
Cu^{+1}	1.076	Zn^{+2}	1.19	Ga^{+3}	1.31	Ge^{+4}	1.43	As^{+5}	1.51	Se^{+6}	1.57	Br^{+7}	1.59
Rb^{+1}	1.137	Sr^{+2}	1.17	Y^{+3}	1.29	Zr^{+4}	1.36	Nb^{+5}	1.43	Mo^{+6}	1.50	I^{+7}	1.54
Ag^{+1}	1.070	Cd^{+2}	1.18	In^{+3}	1.28	Sn^{+4}	1.35	Sb^{+5}	1.43	Te^{+6}	1.47		
Cs^{+1}	1.128	Ba^{+2}	1.13	La^{+3}	1.21	Ce^{+4}	1.26	Bi^{+5}	1.32				
Au^{+1}	1.000	Hg^{+2}	1.14	Tl^{+3}	1.21	Pb^{+4}	1.26						
Anions													
F^{-1}	1.190	O^{-2}	1.26	N^{-3}	1.44	C^{-4}	1.59						
Cl^{-1}	1.126	S^{-2}	1.19	P^{-3}	1.32	Si^{-4}	1.42						
Br^{-1}	1.111	Se^{-2}	1.17	As^{-3}	1.28	Ge^{-4}	1.36						
I^{-1}	1.090	Te^{-2}	1.13	Sb^{-3}	1.20	Sn^{-4}	1.26						

Since the values of ρ_{cat}, when compared along the periods and groups of Mendeleev's system, increase in the directions left to right and bottom to top (Table 1), the structures indicated are found for compounds formed by cations of the first groups having low ρ values with anions having high ρ values. The carbides of elements of the first and second groups are actually acetylides, and contain multiple ions, C_2^{2-}, in which there are covalent bonds between the carbon atoms. For the alkali metals, owing to the considerable predominance of $\rho_{N_3^-}$ over $\rho_{M^{1+}}$, the azides MN_3, containing multiple nitrogen ions, are more stable than nitrides of the normal-valency formula M_3N.

To this group of compounds we may assign also peroxides of metals of the first and second groups and structures having molecular interaction such as the higher peroxides (M_2O_4), polysulfides (M_2S_3), and polyhalides (MX_3) of metals of the first group of the periodic system. The field of existence of structures of this type is characterized by negative values of $(\rho_{cat} - \rho_{an})$ (about -0.3, and more negative values).

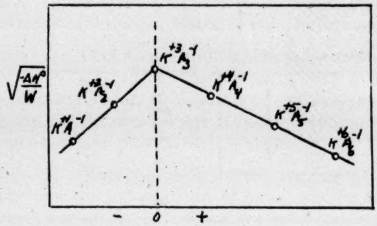

Fig. 1.

The field of ($\rho_{cat} - \rho_{an}$) values ranging from − 0.3 to + 0.1, is characterized by more stable structures of normal valency type in which there is a considerable ionic-bond contribution. The chemical bonds in these compounds are described in Table 2 as ionic. Here we find compounds having nearly equal values of ρ_{cat} and ρ_{an} (Al_4C_3, AlN, MgO, CaS, LiF, NaCl, etc.).

It is probable that certain carbides and nitrides having exceptionally high melting points and considerable chemical stability (SiC, TiN, and others) must be regarded as ionic compounds.

As has been shown in a series of investigations [10] the ions in highly symmetrical lattices of the NaCl or CsCl type may be regarded as undeformed, or as very slightly deformed to a mutually equal extent; the high symmetry of these lattices in itself prevents the development of polarization phenomena [11]. It follows that for compounds in which the values of ρ_{cat} and ρ_{an} are nearly equal and polarization phenomena are not greatly developed, the most "convenient" structures will be highly symmetrical structures of the NaCl or CsCl type. Actually, the majority of compounds described by us as "ionic" have cubic lattices [4,5]. When ($\rho_{cat} - \rho_{an}$) has positive values, greater than about 0.1 (in the case of compounds of elements of the last groups of the periodic table), the most stable structures are either metallic or covalent structures. In this field of ($\rho_{cat} - \rho_{an}$) values, metallic structures are found in compounds having anions with insignificant affinity for an electron (Mn_3C, Fe_3C, Cr_3N, CrN, Mo_2N, MoN, etc.). These structures are characterized by stable metallic cation − cation bonds and weak, evidently essentially covalent, cation − anion bonds.

TABLE 2

Dependence of the Type of Chemical Bond in Binary Inorganic Compounds on the Value of ($\rho_{cat} - \rho_{an}$)

Type of bond	Range of variation of ($\rho_{cat} - \rho_{an}$)	Classes of compounds				
		Carbides	Nitrides	Oxides	Sulfides	Halides
Covalent − ionic	↑ − 0.3	Li_2C_2 (− 0.40) Cs_2C_2 (− 0.46) MgC_2, Mg_2C_3 (− 0.33) BaC_2 (−0.46) YC_2 (− 0.30) LaC_2 (− 0.38)	NaN_3(Na_3N) (− 0.26) CsN_3(Cs_3N) (− 0.31)	(Li_2O_2; Na_2O_2; K_2O_2; K_2O_4; Rb_2O_2; Rb_2O_4; Cs_2O_2; Cs_2O_4; BaO_2)	Li_2S_3; Cs_2S_3	(LiX_3; CsX_3)
Ionic	− 0.3 +0.1	Be_2C (− 0.17) Al_4C_3 (−0.15) SiC (−0.00); TiC (− 0.18); ZrC (− 0.23); VC (− 0.10); NbC (− 0.16); MoC (− 0.09)	Li_3N (− 0.25) Be_3N_2 (− 0.02); Ba_3N_2 (−0.31) AlN (0.00); LaN (−0.23) TiN (−0.03) ZrN (− 0.08) VN (+0.050) NbN (−0.01)	Li_2O (−0.07) Cs_2O (−0.13) MgO (0.00) BaO (− 0.13)	Li_2S (0.00); Cs_2S (− 0.06); MgS (+0.07); BaS (−0.06); La_2S_3 (+0.020)	LiF (0.00); LiI (+0.10); CsF(−0.06); CsI (+0.04) MgF_2 (+0.07); BaF_2 (− 0.06); $CaCl_2$ (+0.06) $BaCl_2$ (0.00)
Metallic or covalent	+0.1 ↓	Cr_3C_2 (− 0.33); Mn_3C (+0.04) Re_4C_3 (?); Fe_3C(?); Co_3C (?); Ni_3C (?)	Cr_3N, CrN (+0.12); Mo_2N, MoN (+0.06); Mn_3N_2; MnN_2 (+0.19); FeN; Fe_4N (?); Co_3N (?); BN (+0.31); $(CN)_2$ (+0.49); Si_3N_4 (+0.15); P_3N_5 (+0.30)	B_2O_3 (+0.49); Al_2O_3 (+0.18); Co_2 (+0.67); SiO_2(+0.33); ZrO_2 (+0.10); P_2O_5 (+0.48); V_2O_5 (+0.23) Nb_2O_5 (+0.17); SO_3 (+0.57); CrO_3(+0.30); MoO_3 (+0.24) Cl_2O_7 (+0.62); Mn_2O_7 (+0.37) OSO_4 (?)	BeS (+0.23); B_2S_3 (+0.36) Al_2S_3 (+0.25); Cs_2 (+0.74); SiS_2 (+0.40); ZrS_2 (+0.17); P_2S_5 (+0.35); MoS_3 (+0.31) Re_2S_7 (?)	BeF_2(+0.23); BeI_2 (+0.33); $MgCl_2$ (+0.13); MgI_2 (+0.17); BF_3(+0.56); Bi_3 (+0.66); $AlCl_3$ (+0.31); AlI_3 (+0.35); CF_4(+0.74); CI_4 (+0.84); SiF_4(+0.40); SiI_4 (+0.50); PF_5 (+0.55); SF_6, S_2F_{10} (+0.64); TeF_6(+0.28); MoF_6(+0.31); OsF_8 (?)

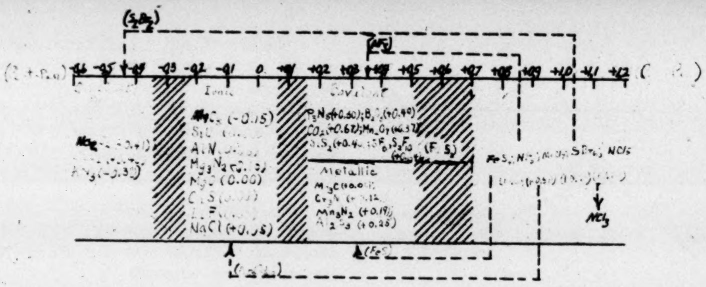

Fig. 2.

In the case of anions having an appreciable affinity for an electron, or of cations that are unable to form metallic bonds, the type of bond found is predominantly covalent (Mn_2O_7, MoF_6, P_3N_5, SF_6, etc.). Among the covalent compounds of this type, owing to the considerable predominance of ρ_{cat} over ρ_{an}, we meet also compounds having stable cation-cation bonds [$(CN)_2$, S_2F_{10}, etc.]. In accord with the powerful development of polarization phenomena occurring in compounds that we have described as "covalent", these have either coordination lattices of low symmetry, the geometry of which permits strong one-sided polarization, or molecular lattices [4, 5, 11]. For values of $(\rho_{cat} - \rho_{an})$ of greater than about +0.5-0.7, the stability of the structures under consideration falls to such an extent that the formation of compounds of the higher valency states of the cation becomes impossible, and this is very clearly manifested, owing to the low ρ-values of the halogens, in the halides of elements of the last groups of the periodic system (large ρ_{cat}) [NF_5(+1.08); NCl_5(+1.14); $MnCl_7$(+0.50); SBr_6(+0.72) etc.].

The stable compounds of these elements having not too large values of $(\rho_{cat} - \rho_{an})$, corresponding to various types of chemical bond, are formed here mainly at the expense of a reduction in the ρ-value of the cation attained by exhibition of a lower valency (the valency $\underline{e}$ of an ion is related to the value of ρ by the equation $\rho = e^{2/(n-1)}$, in which $\underline{n}$ is the Born repulsion coefficient).

This dependence of the type of chemical bond in binary compounds of elements that do not give ions having 18-electron shells on the value of $(\rho_{cat} - \rho_{an})$ is illustrated by the scheme given in Fig. 2. The diffuse passage from one type of bond to another is represented by the wide shaded intermediate zones.

A special group of compounds is formed by elements that give ions having outer shells of 18 electrons. These elements show an enhanced tendency to form covalent bonds: in the whole range of $(\rho_{cat} - \rho_{an})$ it is difficult to find a compound that could be definitely regarded as formed mainly by any other type of bond. The list given below will illustrate this.

Cu_2C_2*	−0.51;	Au_2C_2*	−0.59;	ZnC_2	−0.40;	HgC_2*	−0.45
Cu_3N *	−0.36;	Au_3N *	−0.44;	Zn_3N_2*	−0.25;	Hg_3N_2*	−0.30
GaN *	−0.13;	Ge_3N_4*	−0.01;	ZnO	−0.07;	HgO	−0.12
Ga_2O_3	+0.05;	GeO_2	+0.17;	SnO_2	−0.09;	As_2O_5	−0.25
Cu_2S	−0.11;	Ag_2S	−0.19;	ZnS	0.00;	CdS	−0.01
GeS_2	+0.24;	SnS_2	+0.16;	As_2S_5	+0.32;	Cu_2Cl_2	−0.05
Cu_2I_2	−0.01;	$HgCl_2$	+0.01;	GaF_3	+0.12;	GaI_3	+0.22
$SnCl_4$	+0.22;	$AsCl_5$	+0.58; etc.				

In conclusion I express my deep gratitude to A. F. Kapustinsky for valuable help and advice.

SUMMARY

1. A study has been made of the effect of the relationship between cat and ρ_{an} on the stability of binary inorganic compounds and the type of chemical bond that they contain.

2. Highly stable compounds of normal-valency formula and having bonds of predominantly ionic character may exist only for cations and anions having nearly equal ρ-values.

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* Unstable, explosive compounds.

3. In the case of compounds in which ρ_{an} is considerably greater than ρ_{cat} (high negative values of ($\rho_{cat} - \rho_{an}$)), there occurs a lowering in the stability of compounds of normal-valency formula, and the covalent character of the bonds increases, leading in the limiting case to the formation of multiple anions.

4. The characteristic structures of compounds for which ρ_{cat} is considerably greater than ρ_{an} (high positive values of ($\rho_{cat} - \rho_{an}$)) are those having bonds of metallic or covalent type (sometimes structures containing covalent cation-cation bonds are found). The metallic type of bond is found when the anions have insignificant electron affinity, and the covalent type is found when the anions have considerable affinity for electrons or when the cations are unable to form metallic bonds with one another.

5. Very high positive values of ($\rho_{cat} - \rho_{an}$) result in unstable structures; for such binary compounds stable structures can be found when the cation is in one of its lower valency states. Owing to the reduction in ρ_{cat} the difference ($\rho_{cat} - \rho_{an}$) is reduced to a value that ensures the stability of the compound.

6. The approximate ranges of variation of ($\rho_{cat} - \rho_{an}$), corresponding to the predominance of the various definite types of chemical bond, have been given. The relationships considered refer to binary compounds of elements that do not form ions having 18-electron shells. The elements that give ions having 18-electron shells tend to form covalent bonds and apparently do not form compounds of predominantly ionic character.

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ELECTRONIC PROCESSES IN CHEMISORPTION

COMMUNICATION 1*

F. F. Volkenshtein

In this paper a short exposition will be given of the results of a series of investigations by the author on the theory of heterogeneous catalysis, which have as their object the discovery of the elementary (micro-) mechanism of chemical process occurring at the surface of a crystal. In these investigations the problem of adsorption and catalysis is treated as a problem in physics and is regarded from the point of view of the modern theory of solids. In this paper the whole of the mathematical side of the matter is omitted. We consider here only the main results of our theoretical investigations, and then only from the qualitative side.

Every heterogeneous reaction includes, as obligatory intermediate stages, the stages of adsorption and desorption. The mechanism of a heterogeneous-catalysis process cannot be completely understood without an understanding of its intermediate stages. Hence, although the theory of adsorption can develop outside the theory of catalysis and independently of it, the theory of heterogeneous catalysis, on the contrary, can be built up only in organic association with the theory of adsorption. The construction of a theory of adsorption is the first step in the construction of a theory of catalysis. The present paper is devoted to certain questions in the theory of adsorption (adsorption as a stage of catalysis).

Various types of adsorption exist. The adsorption with which we are concerned in catalysis is generally the so-called "chemisorption", i.e. adsorption due to forces of a chemical nature, in which respect it differs from so-called "physical" adsorption, in which we are concerned with purely electrostatic forces (Van der Walls forces, electrostatic-polarization forces, electrical-image forces).

In their theoretical treatment, physical adsorption and chemisorption require essentially different approaches. In the case of physical adsorption the absorbed molecule and adsorbent can be regarded as two independent systems. The action of adsorbent on the adsorbed substance can be treated as a weak perturbation. In the case of chemisorption the adsorbed molecule and the lattice form a single quantum-mechanical system. The problem cannot now be solved by the methods of perturbation theory.

A solid that is an adsorbent in the process of chemisorption and acts as a catalyst is not an inert (nonparticipating) support on which the chemical processes develop, but is an active participant in these processes, taking part in the intermediate stages of the reaction as one of the components of the reaction. The whole system (reacting molecules plus the solid) must therefore be treated as a single whole.

In such a treatment the electrons of the crystal lattice are found to be direct participants in chemical processes occurring at the surface of the crystal. Moreover, in certain cases they are not only participants, but also regulators of these processes. In this paper we are mainly concerned with the part played by the electrons of the crystal lattice in chemisorption.

Chemisorption can interest us here not only as a stage of catalysis, and not only because it is an essential stage of catalysis, but also for its own sake, since chemisorption is the simplest case of a heterogeneous reaction. It is the reaction consisting in the combination of gas molecules with a solid, with which they form a peculiar unified system.

Chemisorption as a One-electron Bond

First of all let us examine the mechanism of the chemical combination of a gas molecule with a solid. In order to simplify the calculation (it can be made in the general case also), a suitable model must be chosen. We shall examine the simplest case [1, 2]. Let us take as our adsorbate an electropositive univalent atom, denoted by the symbol A. As adsorbent we shall take an ionic crystal formed from singly charged ions M^+ and R^- (M being a metal, and R a metalloid). These ions will be treated as point charges.

We shall introduce also two simplifying assumptions. First, we shall regard the surface of the crystal as an ideal surface. In other words, we shall exclude the existence of defects of various kinds that are bound to exist in and on the surface of every real crystal, disturbing the strictly periodic structure of the lattice. Second, we shall ignore the existence of an electron gas, which is always present in some concentration or other within and on the surface of a crystal. Both of these assumptions will be removed (successively) in further treatment.

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* Paper read at the Conference on Heterogeneous Catalysis, Moscow, January 28, 1953.

In our model we have a one-electron problem. The only electron is the valency electron of atom A. While atom A is sufficiently far from the surface of the crystal, our electron belongs to this atom (Fig. 1, a). When, however, the atom A is on the surface, its electron belongs not only to the atom A, but, strictly speaking, to the system as a whole.

Calculation shows that the valency electron of the atom A is then drawn out into the lattice to a greater or lesser degree. In other words, the electron cloud around the positive core of the atom A, which in the case of the isolated atom has spherical symmetry, is then deformed and to a certain extent drawn out into the lattice. This extension of the electron atmosphere into the lattice forms, in fact, the bond between the adsorbed atom A and the crystal. The bond is thus effected by the valency electron of the atom A. We obtain a bond of the same type as that in the molecular ion H_2^+; it is a one-electron bond (Fig. 1, b).

It can be shown that the strength of the bond between the atom A and the surface depends on how strongly the valency electron of the atom A is pulled into the lattice. The stronger the pull, the stronger the bond. This extension of the electron atmosphere leads, among other things, to the acquiring by the adsorbed atom A of a certain dipole moment, which is of purely quantum-mechanical origin; it is quite different in nature from the dipole moment that arises in physical adsorption and is due to the polarization of the adsorbed atom or molecule by the field of the lattice. We may point out that the value of the dipole moment arising in chemisorption can be shown to exceed, by a factor of several powers of ten, the value of that induced in physical adsorption.

Chemisorption as a Two-electron Bond

The degree of the extension of the electronic atmosphere from the atom A into the lattice is determined both by the nature of the atom A and by that of the lattice. In some cases this extension may be so small, i.e. the bond formed by atom A with the lattice may be so weak, that adsorption due to such a one-electron bond may not occur to an appreciable extent. In this case the free electrons of the crystal lattice itself may come to the rescue. Adsorption may occur by the introduction of a free electron of the lattice into the process.

Let us consider this case [3]. In the preceding calculation we neglected the presence of free electrons in the lattice; it is now necessary to take them into account. Let us return to our model, supplementing it by the introduction of a free electron on the crystal surface. We now have a two-electron problem: the first electron is the valency electron of the atom A, and the second is the free electron belonging to the lattice.

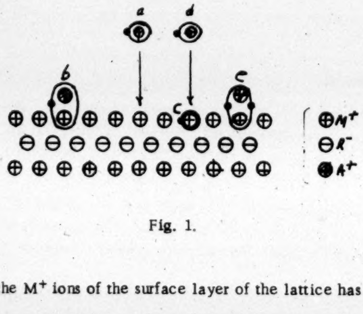

Fig. 1.

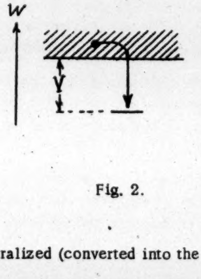

Fig. 2.

What does the presence of a free electron on the crystal surface signify? What does it mean when we say that in the surface conductivity zone there is an electron? It means that there is an electron on one of the surface M^+ ions, or, in other words, one of the M^+ ions of the surface layer of the lattice has been neutralized (converted into the neutral atom M) (Fig. 1, c).

When we say that a free electron moves in the surface conductivity zone, we mean that the electron moves from one M^+ ion of the surface layer of the lattice to a neighboring M^+ ion, and so moves over the surface of the crystal. In other words, we mean that the neutral state of the atom M wanders over the surface by transfer from one M^+ ion to the next.

It can be shown that the atom A, when placed on the crystal surface, creates a local level for the free electron of the lattice. This level is situated below the surface conductivity zone, as shown in Fig. 2. It plays the part of an "attachment" level for the free electron. If the lattice electron falls from the conductivity zone to the local level (as shown diagrammatically by the bold arrow in Fig. 2), this means that the electron has ceased to be free and has become localized on the crystal surface near the place in which A is to be found. The atom A, therefore, plays the part of a "trap" for the free electron. It can be shown that there is then formed a fairly strong two-electron bond between the atom A and the lattice. Two electrons take part in this bond: the valency electron of the atom A and an electron of the lattice itself (borrowed from the family of free electrons).

The electron of the lattice and the atom A are then bound together by exchange forces. In this case these exchange forces are the adsorption forces holding the atom A on the surface and, at the same time, holding the electron of the lattice in the proximity of the atom A. We obtain a bond of the same type as that present in the H_2 molecule. The strength of the bond depends on how far the local level of A is below the surface. The lower the level (the higher the value of V in Fig. 2), the stronger the bond and the stronger the localization of the lattice electron.

As the atom A is removed from the surface of the crystal, the local level in Fig. 2 is drawn toward the zone (V is reduced), the exchange bond between the atom A and the lattice is weakened, and the lattice electron in the local level of A is gradually delocalized, i.e., its wave function becomes more and more smeared out. In the limit, when the atom A is infinitely removed from the surface, the local level is found to be drawn into the zone. The electron in this level is thus taken into the conductivity zone, i.e., completely delocalized and so returned to the family of free electrons.

All this can be graphically redescribed in terms of the model. Let us imagine that the atom A falls on the surface of the crystal, as shown in Fig. 1, *a*. If the free electron of the lattice then remains on one side without forming a link with the atom A, then, in general, adsorption does not occur. We are now ignoring the one-electron bond due to the valency electron of the atom A, as we are considering the case in which this bond is so weak that it may be neglected. If, however, the atom A, on coming to the surface, meets a free lattice electron, as indicated in Fig. 1, *d*, the atom will take up the electron and become adsorbed. The atom A becomes attached to the surface, and the free lattice electron becomes attached to the atom; we obtain a two-electron bond (Fig. 1, *e*).

The free lattice electron acts, therefore, as an adsorption center. Let us state this in another way: a neutral atom M that is present among the M^+ ions of the surface layer serves as an adsorption center. Adsorption of the atom A on such a center results in the localization of this wandering center and consists in the formation of a quasimolecule AM having a characteristic two-electron bond.

The whole of this mechanism, which we have described in the language of the theory of solids, can be described in another, more chemical, language. An electron in the surface conductivity zone may be treated as a free (unsaturated) valency, wandering over the crystal surface. Actually, the metal ion M^+ in the lattice has a complete electron shell, whereas the neutral atom M contains, in addition to the complete shell, a single unpaired electron, i.e. an unsaturated valency. When these two valencies meet, mutual saturation occurs, and this leads to adsorption, i.e. to the chemical combination of the atom A with the crystal.

Activated Adsorption

Let us now examine the consequences ensuing from the concept of free electrons as adsorption centers [4, 5]. Such a treatment of adsorption centers leads us to ascribe a number of specific properties to them: 1) free adsorption centers are not localized on the crystal surface, but wander over the surface; 2) the number of adsorption centers does not remain constant, but increases as the temperature rises; 3) by the action of external factors on the lattice, it is possible (at a given temperature) to alter the number of adsorption centers artificially.

It should be noted that the concentration of electron gas at the surface of an ionic crystal is extremely low under normal conditions. From this it might appear that the surface would be able to accept only a negligible quantity of gas atoms. This, however, is not so: it may be readily shown that, as the surface becomes filled, more and more new adsorption centers arise as a result of transfer of electrons from the normal zone and the formation of a corresponding number of holes.

We shall denote the number of adsorbed atoms per unit area by *N*; the concentration of free electrons in the surface conductivity zone, i.e. the number of free (unoccupied) adsorption centers, by *n*; and the concentration of free holes in the normal surface zone by *n'*. It will be obvious that *n'* is at the same time the total number of adsorption centers (free + occupied). It can be shown that under equilibrium conditions we shall have:

$$\left.\begin{aligned} n &= {}^{1}/_{2}\left(\sqrt{N^2 + 4n_0^2} - N\right) \\ n' &= {}^{1}/_{2}\left(\sqrt{N^2 + 4n_0^2} + N\right) \end{aligned}\right\} \qquad (1)$$

in which n_0 is the concentration of electron (or hole) gas in the case of a clean surface (i.e. when N = 0).

The relations expressed by Equations 1 are represented in Fig. 3. We see that the total number n' of adsorption centers increases as the surface coverage increases, i.e. as N increases, but the number n of free centers slowly falls. We always have a certain reserve of free adsorption centers on the surface which are able to accept gas atoms. It can be shown that, as a result, the differential heat of adsorption, which we shall denote by Q, also depends on the coverage, i.e. on N.

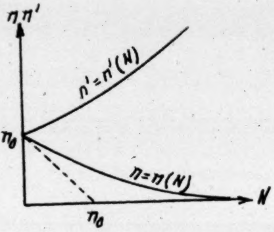

Fig. 3

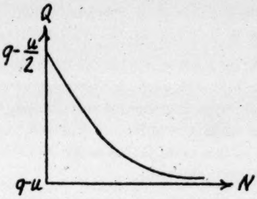

Fig 4

It may be shown that the relation between Q and N is expressed by the formula

$$Q = q - \frac{u}{2}\left(1 + \frac{N}{\sqrt{N^2 + 4n_0^2}}\right) \tag{2}$$

in which q is the heat of adsorption for a separate atom, i.e., the energy of the bond between the adsorbed atom and the adsorption center, and u is the energy of formation of the pair (free electron + free hole), i.e. the work spent in the creation of each adsorption center.

The relation between Q and N, expressed in Equation 2, is represented in Fig. 4. We see that the differential heat of adsorption falls as the coverage increases, in spite of the fact that the surface is assumed to be homogeneous (adsorption centers of one kind only) and the interaction between adsorbed atoms has been ignored.

Let us now turn to the kinetics of adsorption. If adsorption proceeds sufficiently slowly and electron equilibrium in the lattice is established sufficiently rapidly so that electron equilibrium may be considered to exist throughout adsorption process, then for coverage as a function of time we obtain, as can be shown, the following equation, which is valid when the coverage is sufficiently low, i.e. at the beginning of the adsorption process:

$$N = Ae^{-\frac{u}{2kT}}\ pT. \tag{3}$$

(p is pressure, T absolute temperature, and A a constant, which can be analyzed further).

We thus arrive at Benham's law (with the index $\frac{1}{2}$), which often holds in practice and which is generally regarded as a criterion of heterogeneity of surface (in the given case the surface is homogeneous). We see (Equation 3) that heating does not retard the adsorption process, but, on the contrary, accelerates it. We obtain kinetics that are typical of so-called activated adsorption, the activation energy being

$$\epsilon = \frac{u}{2}.$$

To explain the way in which the exponential factor in the kinetic formula (Equation 3) arises — that, practically speaking, is the problem that the theory of activated adsorption sets out to solve. The origin of this factor is generally explained by introducing the concept of a potential barrier on the adsorption curve (Fig. 5). In our case there is no potential barrier. The actual number of adsorption centers, however, rises exponentially with temperature. Here lies the origin of the exponential factor in Equation 3.

In the usual theories of activated adsorption, which are concerned with a potential barrier at the crystal surface, the number of gas atoms striking the surface rises exponentially with the temperature, whereas the number of adsorption centers accepting these atoms remains constant. In our case, on the contrary, the number of accepting centers rises exponentially with the temperature, whereas the number of atoms striking the surface remains practically constant.

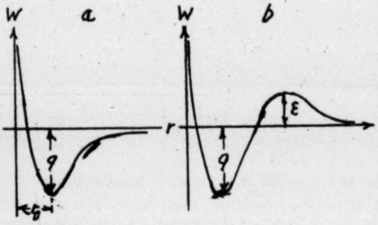

Fig. 5

At a given temperature the concentration of free electrons at the surface of the crystal, i.e. the concentration of adsorption centers, may be artificially changed as a result of external influences affecting the crystal. For example, irradiation of the crystal with photoelectrically-active light should lead to an increase in the adsorbing power of the crystal. Irradiation should also affect the kinetics, bringing about acceleration of adsorption. In fact, while we maintain the irradiation, we at the same time maintain an increased concentration of adsorption centers at the surface of the adsorbent.

Another factor affecting the concentrations of electron and hole gas in the crystal, is provided by impurities. The introduction of foreign donors increases, and the introduction of foreign acceptors diminishes, the concentration of electron gas. Impurities, therefore, should have an effect both on the kinetics of adsorption (accelerating or retarding adsorption) and on the adsorption equilibrium (increasing or diminishing the adsorbing power of the crystal).

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METALLIC COMPOUNDS *

I. I. Kornilov

At the basis of the science of alloys lies Mendeleev's periodic law and Mendeleev's ideas on the nature of alloys, both as solutions and as indefinite compounds [1]. The study of alloys is also one of the main branches of physicochemical analysis, which was founded by Kurnakov [2] and is now being developed in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences under the general direction of Academician Urazov [3]. The chemical side of alloy science was referred to by Kurnakov as chemical metallography [4]. This field of science is now called alloy chemistry, or, as we propose to call it, metallochemistry [5].

The most important objects of metallochemistry are the study of the laws of formation of metal solutions and metallic compounds, and the application of these laws to the determination of the equilibrium diagrams of metal systems. The laws of formation of solid solutions of metals [5, 6, 7, 8], which are based on Mendeleev's periodic law, also relate in equal measure to the formation of metallic compounds. This paper is devoted to some questions relating to the formation of metallic compounds.

Classification of Metallic Compounds

The name "metallic compound" was first introduced by Kurnakov in 1899 when studying compounds formed between metals [9]. Kurnakov's term, metallic compound, is the one that most closely corresponds to chemical views on the nature of alloys. For these compounds, in place of the great variety of terms that are in use – intermetallic compound, "intermediate phase", and others – we consider it correct to preserve the name given by Kurnakov, "metallic compounds" [5].

The most general property of metallic compounds is that they are characterized by the metallic properties inherent in pure metals; they differ from ionic compounds in that the metallic bond is predominant: in metallic compounds atoms of different kinds are linked together in the crystal lattice predominantly by metallic bonds, which, unlike those in solid metal solutions, fix a constant stoichiometric ratio of atoms in the compounds. As a rule, metallic compounds have individual crystal lattices. Atoms of different kinds are arranged in orderly fashion in such a lattice. The strength of the chemical bond between atoms of different kinds in metallic systems that form compounds varies with the composition. This is reflected in the variation of the properties of alloys with concentration and in the nature of the composition – property diagrams. On these diagrams the compositions of compounds are shown as singular points.

Metallic compounds should be classified on the basis of the generally acknowledged classes of chemical compounds proposed by Kurnakov [2, 6]. A great variety of compounds was divided by him into berthollides, compounds distinguished by variable composition and absence of singular points on composition - property diagrams, and daltonides, compounds of constant composition and showing a singular point on composition - property diagrams.

Taking as our basis Kurnakov's principle of classification applied to metallic compounds, we may now single out the large group of compounds formed as a result of transformations of solid solutions. These compounds, which we call Kurnakov compounds (see below), may be of the berthollide or daltonide types. In considering questions concerning the formation of metallic compounds, it must be remembered that there is an undoubted connection between the formation of solid solutions and of metallic compounds. This connection can be readily traced by studying examples of the conversion of solid solutions into Kurnakov compounds and the gradual transition of compounds of the berthollide type into compounds of the daltonide type.

By studies of compounds of constant composition it is possible also to show how a given metal, reacting with elements of different groups of the periodic system, forms compounds of metallic or ionic character.

The enormous ~~range of~~ variation in the chemical nature of solid solutions and metal compounds, which is examined below, is subject to the fundamental principles of Mendeleev's periodic law, and is a consequence of this law. The concept of continuity in solid solutions is closely linked with the discreteness in the composition and properties of metallic compounds of constant composition, and the latter compounds are genetically associated with com-

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* Paper read at a general meeting of the Division of Chemical Sciences of the USSR Academy of Sciences, April 25, 1952.

pounds of the ionic type. This is a graphic proof of the dialectical character of chemical reactions between metals.

Kurnakov Compounds

It has been long established in metallochemistry that many solid metal solutions are stable only at high temperatures: in the course of slow cooling, these solid solutions yield metallic compounds. The classical demonstration of the occurrence of chemical processes in solid solutions was given by Kurnakov in his work on the copper - gold system. For the first time, in 1914, Kurnakov [10] established that when the solid solutions of this system were cooled slowly, two compounds, Cu_3Au and CuAu were formed. In the period of almost forty years that has passed since this discovery, similar compounds have been detected in numerous solid metal solutions. Whereas up to the time of Kurnakov's discovery the system copper - gold, in which these compounds were formed, could be regarded as exceptional, at the present time, on the contrary, a system consisting of solid solutions in which metallic compounds are not formed would be regarded as exceptional. Even in a system consisting of two metal analogs having almost identical atomic diameters, namely silver - gold, it has recently been established (1951) as a result of very long transformation times (about 1340 hours) in the range 300 - 450° that there are signs of the formation of two compounds, Ag_3Au and AgAu [11].

Although it is quite obvious that Kurnakov is the discoverer of metallic compounds in solid solutions, his priority is ignored in many foreign monographs on metallophysics. Foreign scientists call these compounds simply "ordered solid solutions", "arrangement of remote order", "superlattices". These same names have been translated literally into Russian to describe the concept. One is at a loss to understand how our scientists could pass over in silence the ignoring of Kurnakov's priority, when translating a number of monographs into Russian. In Pauling's book "Nature of the Chemical Bond" (translated by Ya. K. Syrkin) there are references to numerous investigations on these questions by foreign scientists, Tammann, Dehlinger, Bragg, Hume-Rothery, and others, but there are no references at all to the first and original investigations of Kurnakov in this field. In the book by Seitz, "Physics of Metals" (translated by E. I. Adirovich and M. P. Shaskolskaya), there are no references at all to Kurnakov's work in the discussions on solid solutions and ordered phases. In the interests of the establishment of the priority of Russian science in the discovery of compounds of these types formed from solid solutions, it will be just to name these compounds "Kurnakov compounds". This general name can replace such indefinite terms as "ordered solid solutions", "superlattice", etc.

Among Kurnakov compounds there is a predominance of compounds of the daltonide type. They are distinguished by rapidity of formation, and characterized by ordered structure, characteristic type of crystal lattice, integral ratio of atoms, and a singular point on a composition-property diagram. These singular points, corresponding to the compositions of Kurnakov compounds, are minima for resistivity and hardness (Fig. 1). The maximum rate of formation of such compounds from solid solutions corresponds exactly to the composition of the compound, and the rate therefore diminishes when one or other component is taken in excess [12].

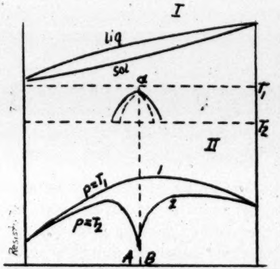

Fig. 1. Melting-point diagram (I) and composition-property diagram (II) for system of continuous solid solutions in which Kurnakov compounds are formed. Resistivity ρ: 1 – at temperature T_1 in the region of solid solutions; 2 – at temperature T_2 in the region of compound formation.

Definite regularities are to be observed in the stability of Kurnakov compounds based on any particular metal. These are determined by the position of the metal in Mendeleev's periodic system. If the temperature of formation of these compounds from solid solutions is taken as a measure of stability, it may be shown that it rises as the difference in the chemical properties of the reacting metals increases.

We may readily convince ourselves of the truth of this by considering, as an example, the formation of compounds from solid solutions of Group VIII metals, which have the greatest tendency to form compounds from continuous solid solutions.

Thus the following Kurnakov compounds are formed from continuous solid solutions of iron with metals of Group VIII: $FeNi_3$, FeCo, $FePd_3$, FePd, and FePt. The formation temperature of these compounds increases regularly from

$FeNi_3$ (580°), through FePd (1120°), to FePt (1320°). This corresponds to the rise in atomic number of the Group VIII element.

If we compare the formation temperatures of Kurnakov compounds of iron with metals of the same row, but of various groups, for example, in the systems: iron - nickel, iron - cobalt, iron - chromium, and iron - vanadium, we can readily convince ourselves of the truth of this rule. In the last two systems also, compounds are formed from solid solutions (FeCr and FeV). The temperature of the formation of these compounds rises from 580° for $FeNi_3$ to 930° for FeCr, and to 1230° for FeV, i.e. rises regularly from compounds of Group VIII elements to those of elements of Groups VI and V.

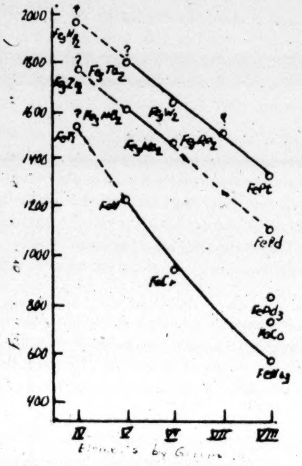

Fig. 2. Variation of the formation and melting points of some compounds of iron with the positions of the elements in the rows of the periodic system.

The relation of the formation temperatures of Kurnakov compounds to the positions of elements in the periodic system, which we were the first to establish, is illustrated by the data given in Fig. 2, in which the formation temperatures of all metallic compounds formed by iron with metals from Group IV to Group VIII are shown. At the moment we are considering the formation temperatures of only Kurnakov compounds.

As will be seen from Fig. 2, a regular rise in the temperatures of formation of Kurnakov compounds occurs in series of iron compounds: from the compound with nickel, through that with palladium, to that with platinum (metals of Group VIII); and from the compound with nickel, through that with chromium, to that with vanadium (metals of Groups VIII, VI, and V).

With increase in the difference in the electronic structures of the metals, corresponding to their increased separation in the periodic system, the temperature stability of the compounds rises, until they become stable right up to the melting point, in which case they are formed directly on crystallization of the melt.

A clear example of such behavior is found in the interaction of iron and titanium (Group IV element). Iron forms only limited solid solutions with this element, and metallic compounds, Fe_3Ti and FeTi, of high melting point are formed directly on crystallization of the melts (see Fig. 2). Hence, with increase in the chemical difference between metals, in accordance with their positions in different groups of Mendeleev's periodic system, the kind of interaction changes. Correspondingly, in metal systems the mutual solubility in the solid state diminishes, and the tendency to form metal compounds directly from melts increases. Hence, the limited solid solutions in metal systems correspond in most cases to the limits of the existence of metallic compounds in these systems, and serve as the boundaries for the transition from solid solutions to metallic compounds. Here in graphic form we see a manifestation of the dialectical law of the transition of quantitative changes into a new quality. The continually rising concentration of the dissolved element and the increase in the strength of the chemical bond at a definite atomic ratio leads to a sudden jump: to the formation, either from solid or from liquid solutions, of metallic compounds of constant composition, having new lattice parameters and new properties. Between solid metal solutions and compounds of constant composition there is, however, an intermediate class of metallic compounds called compounds of variable composition.

Metallic Compounds of Variable Composition (Berthollides)

In metal systems we find compounds that form an intermediate class, which corresponds to their different degree of stability. These compounds differ from solid solutions based on particular metals by having a different type of crystal lattice and a break in continuity of composition. They differ also from compounds of constant composition in that they do not conform to the law of constant and multiple proportions and do not correspond to definite stoichiometric relationships. On composition-property diagrams (Fig. 3) these compounds have no singular points, and their compositions are characterized by a somewhat extensive range of homogeneity. Compounds of variable compositions are not subject to the laws applying to valent compounds.

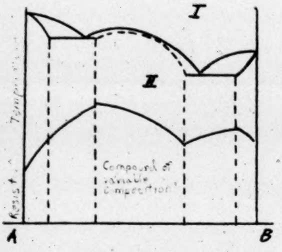

Fig. 3. Melting-point diagram (I) and composition - property diagram (II) for a system in which a compound of variable composition (berthollide) is formed

Substances of this type form an intermediate class of metallic compounds. They are intermediate between continuous solid solutions and metallic compounds of constant composition.

These metallic compounds of variable composition have all the properties of metals. They may therefore be called metallic compounds of variable composition (berthollides).

The formation of such compounds is again related in periodic fashion to the distribution of the elements by groups, and to the ratio of atomic diameters and of concentrations of valency electrons. The type of the crystal structure of such compounds is often determined by the ratio of the number of valency electrons to the total number of atoms in the elementary cell. These compounds have therefore been called "electronic compounds". The laws of their formation have been studied by Konobeevsky [13] and other investigators.

In many metallic compounds of variable composition, such as the β-phase in the copper-zinc, silver-zinc, and other systems, the features characteristic of variable composition are preserved only at high temperatures. At lower temperatures, these berthollide phases of variable composition yield Kurnakov compounds having ordered dispositions of atoms in their lattices and characteristic singular points on composition - property diagrams. An example of such a compound is the CuZn, or so-called β-phase, in the Cu-Zn system [14]. The most typical transformation of this sort is that of the β-phase in the silver-Zn system into a Kurnakov compound corresponding in composition to AgZn.

An interesting example of the transformation of compounds of variable composition into a Kurnakov compound is that of the γ-phase of variable composition in the aluminum-magnesium system into the compound of constant composition Al_3Mg_4, as established by Mikheeva [15]. The author writes that at low temperatures the γ-phase is the carrier of the compound Al_3Mg_4, which only at high temperatures, close to the onset of melting, is in the state of complete dissociation.

In the course of the gradual transition from compounds of variable composition to compounds of constant composition, a new transitional class of metallic compounds makes its appearance. These compounds are characterized by the formation of peculiar crystal structures, in which the valency of atoms of a given element changes as the composition of the solid phase changes. Typical examples of such compounds are those having the so-called nickel arsenide structure (NiAs). This "homologous group of phases", as Makarov calls it [16], is characterized by a variable number of atoms in the elementary cell, corresponding to a continuous change in the valencies of the atoms as the composition of the given phase changes. It should be noted that compounds of this sort do not lose their metallic properties and therefore can be called metallic compounds.

Metallic Compounds of Constant Composition (Daltonides)

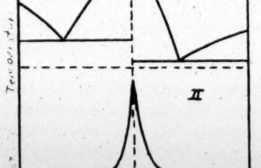

Fig. 4. Melting-point diagram (I) and composition-property diagram (II) for a system in which a compound of constant composition (daltonide) is formed

The most typical metallic compounds of constant composition having whole-number ratios of atoms are formed between electropositive and electronegative elements. It was with these compounds that Kurnakov began his systematic investigations of compounds between metals, and it was to these that he first applied the name of "metallic compounds" [9]. These compounds are formed between, for example, an alkali or alkaline-earth metal and a more electronegative metal of Groups IV B, V B, or VI B.

Compounds of this type are formed directly from liquid solutions. On melting-point diagrams they show maxima, and their compositions correspond to whole-number ratios of atoms. On composition-property diagrams these compounds show singular points (Fig. 4), corresponding to the constant compositions of the compounds. Compounds of this type were called "daltonides" by Kurnakov [2].

Unlike Kurnakov compounds, such metallic compounds, when they do not form solid solutions with the components, show a maximum resistivity and hardness (see Figs. 1 and 4). The resistivity of such compounds is sometimes 500-1000 times as great as the same property for the components (in the case of Mg_2Sn, for example). This indicates the reduction of the number of free electrons and the formation of a bond by the valency electrons.

The relative stabilities of compounds of constant composition, like that of Kurnakov compounds, is determined by the chemical properties of the interacting metals and depends on their positions in the periodic system. If in this case we take the melting point of a compound (the temperature of its formation from liquid solution) as a measure of the relative stability of the bond it contains, then the existence of such a relationship can be shown by an examination of a large number of metal compounds. For example, by an examination of the compounds of magnesium we may show how their melting points vary according to the position of the second element in the Groups, and how the gradual quantitative change in the character of the chemical bond in metallic compounds results in a new quality: in a transition to compounds of the ionic type. The metallic compounds of magnesium were studied systematically by Stepanov [17].

In Fig. 5, on the left, melting-point curves of metallic compounds of magnesium with elements of Groups IB, IIB, and IIIB are shown. We may conclude from these curves that the formation temperature or stability of compounds of magnesium with elements of all three groups rises as the atomic number increases. The position is particularly clear for compounds with elements of Groups I and II, and as regards the Group III elements, although there are no experimental data on the formation temperatures of the compounds Mg_3In_2 and Mg_3Ga_2 (arbitrary values are given), it may be assumed that the order shown will be confirmed in the future.

The curves on the right of Fig. 5 relate to compounds of magnesium with elements of Groups IV B, V B, and VI B. An analysis of data on compounds formed by magnesium with elements of these groups indicates that these compounds are subject to valency rules. As the number of the group increases, they gradually pass over into ionic compounds.

For the final establishment of the relation between the melting points of these compounds and the positions of the reacting elements in the periodic system, the necessary complete experimental data are unfortunately not available. Information is available on the melting points of all compounds of magnesium with elements of Group IV and of individual compounds of magnesium with elements of Groups V and VI. An examination of compounds formed with elements of Group IV, which are of the Mg_2R type, shows that the formation temperature of these compounds falls as the atomic number of the reacting element rises. The same order is found for the compounds of the type Mg_3R_2, formed with the Group V elements bismuth and antimony. The absence of data on the temperatures of formation of compounds of magnesium with arsenic, phosphorus, nitrogen, and sulfur and its analogs makes it impossible to reach a final conclusion regarding the role of the elements of Groups V and VI. Nevertheless, it may be assumed that the melting points of compounds of magnesium with these elements will fall as the atomic number of an element of a given group increases.

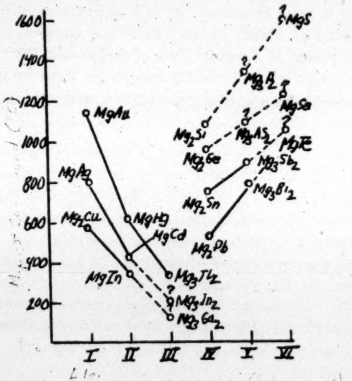

Fig. 5. Dependence of the melting points of some magnesium compounds on the positions of elements in the rows of the periodic system.

All compounds formed by magnesium with elements of Groups I-III have metallic properties: they are metallic compounds. Metallic properties are possessed also by compounds of magnesium with Group IV elements, and the same properties are characteristic of the majority of the compounds formed by magnesium with Group V elements.

Compounds of some Group VI elements, such as sulfides, selenides, and tellurides of magnesium, which are to a considerable extent ionic compounds, still preserve certain metallic properties. Compounds of this type belong to the class of so-called semiconductors. Compounds formed by magnesium with halogens (Group VII) are purely ionic compounds: the metallic character of the bond has completely disappeared, and they are classical examples of salts.

Thus, by an examination of compounds formed by magnesium with elements distributed over the various groups of the periodic system, we may convince ourselves of the gradual change of the metallic character of the bond in these compounds and their transition to ionic compounds: a transition from purely metallic magnesium compounds to magnesium salts.

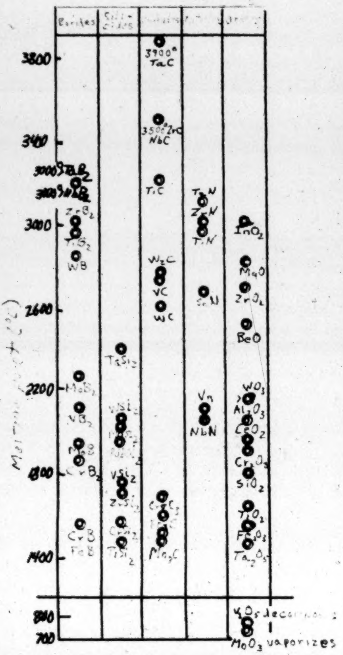

Fig. 6. Melting points of the borides, silicides, carbides, and nitrides of some metals of the transitional groups of the periodic system

The dependence of the relative stabilities of metallic compounds formed from melts on the positions of the reacting elements in the periodic system can be demonstrated also by examples based on compounds of other metals. We have examined above the dependence of the formation temperatures of Kurnakov compounds (the example taken being iron) on the positions of the elements in the various groups (Fig. 2). In Fig. 2 data are given also of the melting points of compounds formed by iron with metals of Groups IV-VIII. The three curves given in Fig. 2 for elements of the 4th, 6th, and 8th rows, uniting points representing the melting points of compounds of iron with Group IV-VIII metals, prove convincingly, in spite of the absence of some experimental data, that this relationship holds. The melting points of metallic compounds of iron rise regularly from Group VIII to Group IV and, in each group, from low to high atomic number. The relative similarity or difference between the two components determines whether the formation of the iron compound occurs from solid solutions or directly on crystallization.

Very clear examples of the dependence of the melting points of the metallic compounds on the positions of the reacting elements in the periodic system are afforded by compounds formed by transition-group metals with nonmetals: boron, silicon, carbon and nitrogen. Compounds of this type belong to a special class of compounds, the majority of which form so-called interstitial phases [18]. These compounds have very high melting points and high hardness, and they all have metallic properties.

In Fig. 6 data are given on the melting points of some compounds formed by these metals with boron (borides), silicon (silicides), carbon (carbides), and nitrogen (nitrides). It will be seen from these data that a general law is observed by the melting points of these compounds: the melting points of these metallic borides, silicides, carbides, and nitrides rise regularly in a given group of elements as the atomic number of the element increases (Fig. 6). For example, chromium boride has a lower melting point than molybdenum boride, and molybdenum boride has a lower melting point than tungsten boride. The carbides of these metals have the highest melting points, the carbides of elements of higher atomic number having the higher melting points.

The questions relating to the formation of metallic compounds that we have examined above form part of the general problem of inorganic compounds. As we have shown above, the chemical interactions of metals are characterized by a number of transitional stages: from solid metal solutions to metallic compounds of variable and constant composition, and from these to compounds of the ionic type. This evolution by gradual transition from the metallic type of bond to the ionic type is characterized also by sudden jumps that form a manifestation of the dialectical law of the transition of quantitative changes into a new quality. All this arises from the chemical properties of the elements, which are based on Mendeleev's periodic law.

The solution of these general problems is of great importance for the establishment of the general laws of the formation of solid metal solutions and metallic compounds. These investigations are important also in the study of simple and complex phase diagrams of metal systems. They serve as a basis for the prediction of the types of phase diagram not only of binary, but also of many ternary, quaternary, and more complex metal systems, the great majority of which have not been studied experimentally.

SUMMARY

1. The chemical interaction between metals or between metals and metalloids, which results in the formation of various substances having metallic properties, is characterized essentially by the formation of metallic solutions

and metallic compounds.

2. The chemical resemblances and differences between metallic elements, which are associated with the dispositions of the elements in the same or different groups of the periodic system, are the fundamental factors determining the possibility of the formation of solid metal solutions in some cases and metallic compounds in others.

3. In accord with the teachings of Mendeleev and Kurnakov concerning solutions and compounds, it has been shown that there is a close relationship between metallic solutions and metallic compounds. These two kinds of interaction between metals must be regarded in their essential unity. The fundamental laws of dialectical materialism – the transition of quantitative changes to a new quality, and the unity of opposites – are manifested in graphic form in the transitions of metallic solutions and metallic compounds.

4. The name "metallic compound", first introduced by Kurnakov in 1899, is the most satisfactory designation for those products of the chemical interaction of metals which, their great variety notwithstanding, are distinguished by one fundamental feature, the metallic character of the bond. The name "metallic compound" must be substituted for many indefinite foreign terms that were brought into Soviet science without adequate critical examination, e.g. intermetallic compounds, intermediate phases, secondary solid solutions, etc.

5. With the object of gaining the acknowledgement of the priority of Russian science in the discovery of metallic compounds formed as a result of thermal transformations of solid solutions, it is proposed to call them "Kurnakov compounds". since Kurnakov was the first to establish, in 1914, the formation of such compounds in the system gold-copper, a phenomenon that has since been observed in practically all solid metal solutions.

6. With increase in the chemical difference between metallic elements, as deduced from their positions in different groups of Mendeleev's periodic system, the kind of interaction characterizing the formation of solid solutions gradually passes over to the formation of metallic compounds from liquid solutions.

7. The stability or strength of the bond between atoms of different elements in metallic compounds determines the temperature at which the compounds are formed: the more stable the compound, the higher the formation temperature. It has been shown by an examination of some metallic compounds of magnesium, iron and transitional-group metals, that the stability and the formation temperature of a compound rise as the difference in the chemical properties of the elements increases.

8. The laws of formation of metallic solutions and metallic compounds are important for the theoretical determination of the nature of the interaction of metals and the prognosis of the types of phase diagrams that will be found in systems not yet studied. This method of predicting the as yet unstudied phase diagrams of simple and complex metal systems, which is on principle possible, is of great importance, not only for the study of metals now widely employed in practice (iron, nickel, aluminum, etc.), but also for the study of metals forming equilibrium systems that have as yet received little or no study. These metals include chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, and hafnium.

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LIMITING CURRENTS ASSOCIATED WITH THE CATALYTIC DISCHARGE OF HYDROGEN IONS IN PRESENCE OF AMINES

COMMUNICATION 2. CATALYTIC EFFECT OF QUININE

S. G. Mairanovsky

In the present paper we give the results of an experimental verification of the theory developed previously [1]. The main subject for investigation has been the catalytic action of quinine in presence of hydrochloric acid as a proton donor. Quinine is one of the most active catalysts [2], and considerably reduces the hydrogen overvoltage: its catalytic wave does not merge with the background even at pH < 1, and can be detected at a quinine concentration of $1 \cdot 10^{-6}$ M.

Hydrochloric acid provides only one kind of proton donor, the concentration of which is readily calculated, but in buffered solutions, which have been used by other authors [3, 4], the phenomena are complicated by the presence of several kinds of donors and by the kinetics of the conversion of one kind into another at the electrode surface [5, 6].

All measurements were carried out in N LiCl as supporting electrolyte. This high concentration of indifferent electrolyte enabled us to neglect changes in the ionic strength of the solution when working with various concentrations of hydrochloric acid.

EXPERIMENTAL

Materials. The quinine used in this work was the monohydrochloride, m.p. 159°. Its concentration in the original solutions was determined by amperometric titration with hydrochloric acid. The hydrochloric acid ("chemically pure" brand) was used in the form of 0.1 N and 0.5 N solutions, and its polarographic purity was checked by polarography of solutions neutralized with caustic potash ("pure for analysis" brand). In calculating the concentration of hydrochloric acid in the polarographic solutions, a correction was made for the neutralization of the second equivalent of quinine. The lithium chloride ("chemically pure" brand) was checked for polarographic purity. Its solutions were not strictly neutral, and the original solution (2N) was therefore neutralized with hydrochloric acid until a just-perceptible hydrogen wave appeared in a polarographic test of the solution (galvanometer sensitivity 10^{-8} amp per division). The remaining reagents used in the work were ammonium chloride, "pure for analysis"; semicarbazide hydrochloride, "pure for analysis"; and pyridine base, "chemically pure", distilled.

Apparatus. The experiments were carried out on a visual polarograph at 25 ± 0.2°. In order to increase the accuracy of readings, the oscillations of the galvanometer were damped by Skobets and Kavetsky's method [7]. The mercury at the bottom of the vessel served as anode. The characteristics of the capillary of the dropping electrode were as follows: $m = 2.70$ mg·sec.$^{-1}$, $t = 0.20$ sec., $m^{2/3} t^{1/6} \doteq 1.47$ mg$^{2/3}$ · sec$^{-1/2}$. The values of the limiting currents were not adjusted to $m^{2/3} \cdot t^{1/6} = 1$. The heights of the waves were corrected for residual current. Air was removed from the solutions investigated by passage of hydrogen, which was given a preliminary passage through N LiCl at 25°.

RESULTS OF EXPERIMENTS

A number of polarograms obtained at various quinine and hydrochloric acid concentrations are given in Figures 1 and 2. The abscissas are values of potentials in volts referred to the potential of mercury in N LiCl. The values of the potentials are not corrected for the ohmic potential drop in the cell and galvanometer. The ordinates are values of current in microamp. It will be seen from Figures 1 and 2 that the polarograms have two waves, the first of which occurs at less negative potentials and corresponds to the catalytic wave, while the second corresponds to the usual discharge of hydrogen ions. The height of the composite wave corresponds to the diffusion current of hydrogen ions.

Experiments at Constant HCl Concentration. In Fig. 1 and Table 1 results are given of some experiments at various concentrations of quinine and almost constant concentrations of hydrochloric acid.

The results show that at first the limiting catalytic current rises with increase in the quinine concentration; the rate of rise then becomes less, and the current tends to a definite limit. It is not difficult to see that this limit is the value of the hydrogen ion diffusion current $\kappa_{DH^+}[DH^+]_0$. The limitation of the growth of the catalytic wave is therefore of a diffusional nature. As the concentration of acid in the solution is increased, the limit to the growth of the catalytic current moves upward.

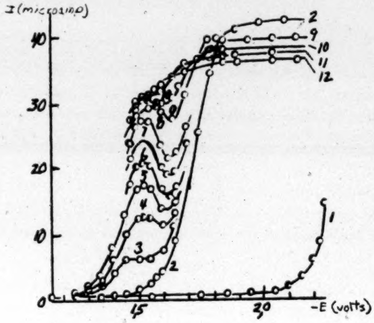

Fig. 1. Catalytic waves in presence of HCl for different concentrations of quinine: 1) residual current (N LiCl); 2) $6.8 \cdot 10^{-3}$ N HCl; 3-12) curves of the catalytic current for rising concentration of quinine.

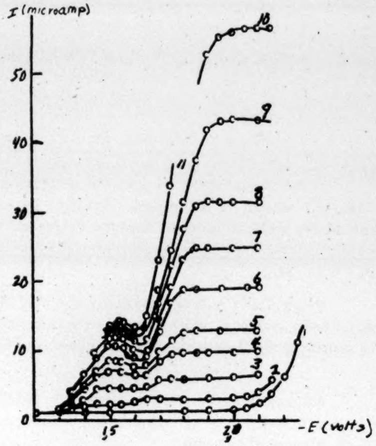

Fig. 2. Catalytic curves produced by quinine at different concentrations of hydrochloric acid: 1) supporting electrolyte (N LiCl); 2-11) acid concentration rises from 2 to 11.

If, after the limit associated with the diffusional restriction of hydrogen ions has been attained, increase in the quinine concentration continues, then at more negative potentials a new wave (Fig. 3), similar in form to the catalytic wave, makes its appearance. It is possible that this wave is the result of catalytic discharge of hydrogen, in which water molecules serve as proton donors.

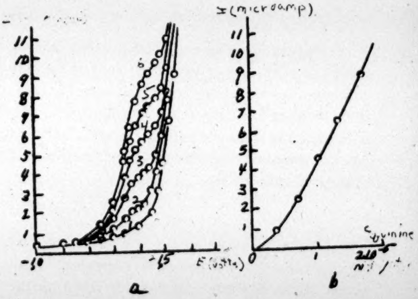

Fig. 4. Limiting catalytic current in presence of 0.05 N HCl. a) Polarograms for different quinine concentrations (in 10^{-6} M): 1) 0; 2) 3.55; 3) 7.1; 4) 10.6; 5) 14.2; 6) 17.7; b) dependence of $i_{\text{lim.}}$ on the quinine concentration.

Experiments at Constant Quinine Concentration. In Fig. 2 are given the polarograms, and in the first columns of Table 2 are presented the experimental results, obtained at different acid concentrations and at approximately constant catalyst concentration.

TABLE 1

Dependence of Limiting Catalytic Current on Quinine Concentration

Concentration		i* expt. (micro-amp)	$\kappa_{DH^+}[DH^+]_0$ (microamp)	i calcd. (microamp)	Concentration		i expt. (micro-amp)	$\kappa_{DH^+}[DH^+]_0$ (microamp)	i calcd. (microamp)
Quinine (10^{-5} M)	HCl (10^{-3} M)				Quinine (10^{-5} M)	HCl (10^{-3} M)			
1.36	3.65	4.2	22.3	4.34	1.41	6.78	5.42	41.3	5.32
2.72	3.63	8.5	22.1	7.92	3.10	6.71	11.6	40.9	12.3
4.06	3.59	11.4	21.9	11.1	4.43	6.69	16.3	40.7	16.5
5.40	3.57	12.5	21.8	13.0	6.34	6.64	19.4	40.4	20.7
6.70	3.53	14.5	21.6	14.2	8.50	6.55	24.0	39.9	24.0
9.30	3.48	15.6	21.2	15.7	11.1	6.47	26.3	39.4	26.6
11.8	3.42	16.3	20.9	16.5	16.5	6.29	29.1	38.3	29.4
14.3	3.37	16.8	20.5	16.9	21.5	6.13	29.8	37.4	30.2
28.0	3.28	17.0	20.0	17.1	26.5	5.98	30.6	36.5	31.1
31.6	3.21	17.1	19.6	17.3	36.0	5.74	31.8	35.0	31.3

**i* is the limiting catalytic current

The results show that at first the catalytic current increases proportionally to the rise in acid concentration; the rate of increase then becomes less, and finally, at a sufficiently high acid concentration, the current tends to a limit determined by the catalyst concentration. The higher the concentration of catalyst, the higher the limiting catalytic current and the higher the acid concentration required for its attainment. As the limit to the rise in catalytic current occurs at relatively high acid concentrations, it may be supposed that this limit is associated with the filling of the electrode surface with hydroxonium ions, which do not succeed in becoming catalytically discharged at low quinine concentrations.

TABLE 2

Dependence of the Limiting Catalytic Current on the Acid Concentration

Concentration		i* expt. (micro-amp)	b (liters/mmole)	i calcd. (microamp)	Concentration		i expt. (micro-amp)	b (liters/mmole)	i calcd. (microamp)
Quinine (10^{-5} M)	HCl (10^{-3} M)				HCl (10^{-3} M)	Quinine (10^{-5} M)			
0.47	3.30	1.12	3.0	1.36	0.46	7.90	1.59	2.9	1.75
0.95	3.29	3.74	1.0	3.83	1.09	7.86	4.4	0.76	4.57
1.45	3.27	5.6	0.54	5.36	3.09	7.70	13.4	0.71	13.4
1.93	3.26	7.2	0.44	6.57	4.50	7.60	18.5	0.61	17.7
2.90	3.23	8.9	0.62	8.50	5.96	7.48	22.1	0.62	21.4
3.93	3.20	10.4	0.64	10.0	7.46	7.37	22.4	0.85	24.3
4.96	3.14	11.5	0.64	11.1	8.95	7.23	25.6	0.76	26.9
6.93	3.10	12.7	0.67	12.5	10.2	7.12	26.9	0.77	28.3
9.12	3.05	13.3	0.71	13.3	11.5	7.03	28.4	0.75	29.5
16.8	2.78	13.3	0.78	14.25	14.1	6.85	30.1	0.76	31.4
–	–	–	–	–	26.5	6.66	30.7	0.77	32.6
–	–	–	–	–	23.0	6.15	30.5	0.80	33.6

Experiments in Presence of 0.05 N HCl. In Fig. 4 a polarograms obtained in presence of 0.05 N HCl are given, and in Fig. 4 b the points show the dependence of the limiting catalytic current on the quinine concentration. The form of this curve is somewhat unusual: it is convex with respect to the axis of abscissas. Its slope falls with increase in the concentration of catalyst, falling to zero at sufficiently high concentrations, so that the curve becomes a straight line. This kind of relationship between the current and the catalyst concentration may be observed also for other amines, as can be seen from Kirkpatrick's graphs [3]; Kirkpatrick, however, attached no importance to this phenomenon and does not mention it in the text.

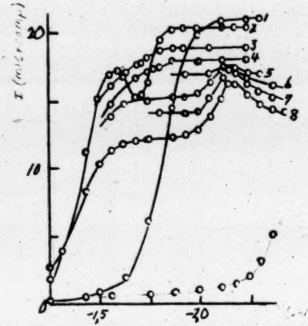

Fig. 3. Appearance of a second catalytic wave due to quinine [quinine concentration (c_q) in 10^{-4} M; HCl concentration (c_{HCl}) in 10^{-3} M] 1) $c_q = 0$, $c_{HCl} = 3.27$; 2) $c_q = 1.1$, $c_{HCl} = 3.16$; 3) $c_q = 1.97$, $c_{HCl} = 2.91$; 4) $c_q = 2.83$, $c_{HCl} = 2.82$; 5) $c_q =$ $= 3.5$, $c_{HCl} = 2.60$; 6) $c_q = 4.67$, $c_{HCl} = 2.30$; 7) $c_q = 5.64$, $c_{HCl} = 2.14$; 8) $c_q = 7.36$, $c_{HCl} = 1.78$.

DISCUSSION OF RESULTS

The equations that we have introduced are in agreement with the experimental results obtained at various quinine and hydrochloric acid concentrations. The experimental results enable us to evaluate the constants occurring in these equations.

Experiments at High Acid Concentration. From Equations 30 and 31 of the previous communication [1]* it follows that

$$rp = 2 / \kappa_B. \tag{44}$$

Assuming that $\kappa_B = 2.33$ microamp · mmole/liter, as found from data on the electrical conductivity of quinine [8], we obtain the value of 0.86 mmoles/microamp · liter for rp. Substitution of the value of rp and experimental values of $\underline{i}$ and $[K]_0$ (Fig. 4) in Equation 41 yields several systems of equations. Solution of these systems gives $Q^1 = 1030$ microamp · liter/mmole for $[DH^+]_0 = 50$ mmoles/liter) and $\underline{r} = 1.1 \cdot 10^{-5}$ mmoles/liter. Equation 44 gives the value $7.8 \cdot 10^4$ microamp^{-1}.

These values of the constants were used in constructing the theoretical curve $i = f\,[K]_0$ from Equation 42. The curve is shown in Fig. 4 b.

The character of the dependence of the current on the quinine concentration at low values of the latter may be explained on the basis of the mechanism discussed in the first communication [1] for the formation of the catalytic current. At very low catalyst concentrations the slowest stage is the process III, the interaction of uncharged complexes [1]. Owing to the slow rate at which they interact and their comparatively high rate of formation, the proportion of uncharged complexes in the total surface concentration of catalyst may be fairly high. These complexes form the passive part of the surface concentration of catalyst, taking no direct part in the catalytic process. The rate at which the passive part of the catalyst is converted into active catalyst, i.e., the rate of the interaction of the complexes, depends on the square of the surface concentration of these complexes. This rate is also essentially determined by the value of the catalytic current at very low values of $[K]_0$. As the concentration of catalyst increases, the rate of interaction of the complexes increases more rapidly than their rate of formation, and the proportion of them in the total surface concentration rapidly falls. As a result, the slowest stage, determining the value of the catalytic current, becomes the direct process (I), the rate of which varies linearly with the active part of the surface concentration of catalyst. Further increase in the concentration of the catalyst lowers the proportion of passive catalyst to such an extent that it may now be neglected in comparison with the total surface concentration. In this case the relationship between the catalytic current and the catalyst concentration becomes a linear one (with a proportionality coefficient of Q').

Dependence of the Limiting Current on the Acid Concentration. The dependence of limiting currents on proton-donor concentrations is shown in Fig. 5. The points correspond to the experimental values of the current (see Table 2). For the catalytic waves the points are extrapolated linearly to the same concentration of quinine. The values of currents lying on the straight line correspond to the height of the composite wave, i.e. to the value of the hydrogen diffusion current. The slope of the straight line gives the value $\kappa_{DH^+} = 6.1$ microamp · liter/mmole for hydrochloric acid in N LiCl ($m^{2/3} \cdot t^{1/6} = 1.47$ mg$^{2/3}$ · sec$^{-1/2}$). The assemblies of points along the curves give the experimentally found dependence of the catalytic current on the hydrochloric acid concentration. Theoretically, this relationship is given by Equation 33, which represents the observed facts fairly well.

At a sufficiently low concentration of proton donor, the curve for the limiting catalytic current practically coincides with the straight line representing the dependence of the diffusional, noncatalytic current due to hydrogen-ion discharge on the donor concentration (Fig. 5).

It is not difficult to see that the field of donor concentrations within which the two lines become coincident grows as the catalyst concentration rises. The explanation of this is that at low donor concentration all the particles of donor that reach the electrode surface are "dealt with" by the catalyst. It is obvious that the higher the concentration of catalyst, the greater will be the amount of donor that it can "deal with" completely. As the content of donor in the solution is increased, the value of the catalytic current becomes less than the total current due to the discharge of hydrogen ions. This means that the catalyst will no longer be able to "deal with" the whole of the donor that arrives at the electrode. With further increase in donor concentration, the rate of rise of the catalytic current will become lower and lower, and will tend to some limiting value determined by the concentration of the catalyst and its capacity for dealing with donor. Equation 33 is transformed, first into Equation 37, and, finally, with further increase in the concentration $[DH^+]$ into Equation 34.

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* The numbering of the equations is the same for both communications.

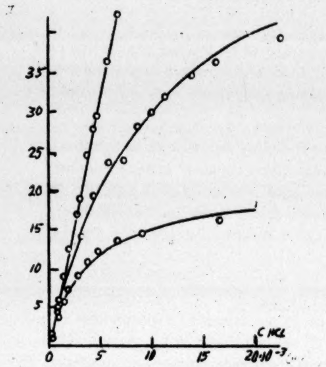

Fig. 5. Dependence of limiting currents on the concentration of hydrochloric acid: 1 and 2 – catalytic currents at quinine concentrations of $3.3 \cdot 10^{-5}$M and $7.9 \cdot 10^{-5}$M respectively; 3 – diffusion current of hydrogen discharge

The donor concentration at which the limit of rise of the catalytic current is practically attained is determined by the value of the coefficient b. The value of b can be determined from the experimental data by substituting them in Equation 33. For this purpose it is convenient to modify Equation 33 to some extent. Let us write

$$K_1 a_B a_{DH^+} sF = R \qquad (45)$$

Taking Equation 40 into account, we obtain

$$i = \frac{\kappa_{DH^+}[DH^+]_0 R([K]_0 - r \quad ip)}{\kappa_{DH^+}(1 + b[DH^+]_0) + R([K]_0 - r \quad ip)} \qquad (46)$$

and from Equation 46 we obtain

$$b = \frac{R([K]_0 - r \quad \sqrt{ip})(\kappa_{DH^+}[DH^+]_0 - i) - \kappa_{DH^+}}{\kappa_{DH^+}[DH^+]_0 \cdot i} \qquad (47)$$

When the experimental values given in Table 2 were substituted in Equation 47, a series of equations was obtained which permitted the values of b and R to be found. The values of b and R so found were not strictly constant: they varied within certain limits according to the acid/quinine concentration ratio.

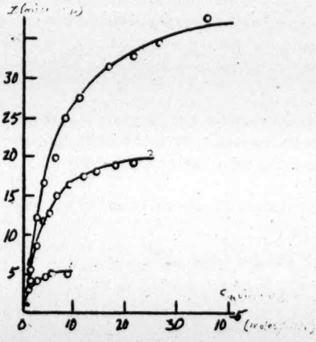

Fig. 6. Dependence of the limiting catalytic current on the quinine concentration; hydrochloric acid concentrations in 10^{-3}M: 1 – 1.06; 2 –3.65; 3 – 6.8

We may assume, for simplicity, that the discrepancies in the values of b and R, determined from Equation 47, are due to the variable nature of b. Substituting the mean value of b (0.7 liter/mmole) and the value Q' = 1030 microamp·liter/mmole (in 0.05 N HCl) in Equation 39, and applying also Equations 36 and 45, we find that Q = 1060 microamp.liter/mmole and R = 740 microamp·liter²/mmole². The value of R was substituted in Equation 47, and from the experimental data a series of values of b for various values of $[DH^+]_0/[K]_0$ was found. These values are given in the fourth column of Table 2. At relatively high and low concentrations the value of b is somewhat higher than at moderate concentrations, where it is approximately constant. The increase in the value of b arises from the fact that the value of the catalytic current is lower than that derived from our equations.

The lowering of the value of the catalytic current at very low acid concentrations may be explained as follows. Apart from diffusional restrictions, which are taken into account in the derivation of the equations by means of the constant κ_{DH^+}, in the case of a catalytic process there is a further retarding factor. The essential point is that it is not sufficient for the proton donor to come to the electrode surface, it must then move a certain distance over the surface until it meets a catalyst molecule. The effect of such "sliding about" will be particularly notable at low donor concentrations, when the slowest stage, which determines the value of the catalytic current, is the supply of proton donors to the catalyst. As the concentration of donor increases, the slowest stage becomes the action of the catalyst on the donor, and the effect of sliding becomes inappreciable.

A certain rise in the value of b at high acid concentrations may be explained by the fact that in this case each catalyst molecule has to deal with close to the maximum amount of donor and therefore causes the evolution of a large amount of molecular hydrogen, which, not being able to escape sufficiently rapidly from the electrode, hinders the approach of donor to catalyst.

The last column of Table 2 contains values of limiting currents calculated by Equation 46 by substitution of R = 740 microamp · liter^2/mmole^2 and b = 0.7 liter/mmole. At the same time, in order to avoid cumbersome calculations, a rounded value of the experimental current was placed under the root sign in Equation 46. It will be seen, by a comparison of values of the current calculated and found experimentally, that the discrepancies between them, in spite of the great variation on the value of b, are comparatively small. Exceptions are formed by values of currents at low acid concentration.

Dependence of the Value of the Limiting Current on the Catalyst Concentration. The variation of the limiting current with the quinine concentration is shown in Fig. 6. The points correspond to experimental values (Table 1) linearly extrapolated to the same acid concentration. It will be seen from the figure that, as the quinine concentration increases, the current tends to a definite limit, which, as already pointed out, is determined by the rate at which hydrogen ions are presented to catalyst molecules at the electrode surface. This same inference follows from analysis of Equation 46. As the concentration of the catalyst is increased, the second term of the denominator of the expression in Equation 46 increases, so that, when a certain concentration of quinine is attained, the value of the first term can be neglected in comparison with the second, and Equation 46 becomes $i = \kappa_{DH^+}\ [DH^+]_0$.

The calculated values of the currents (last column, Table 1) agree with those found experimentally. The curves presented in Fig. 6 are constructed from Equation 46 (R = 740 microamp · liter^2/mmole^2 and b = 0.7 liter/mmole). The experimental points fit very well to these curves.

Determination of the Value of the Catalytic Current. Calculation shows that, if for the catalytic current we take not the value i_m, but its true value i_1 (see Fig. 1 of the previous communication [1]), then the variation in the value of b (for a corresponding value of R) is greatly reduced, and the agreement between calculated and experimental values of the current is very much improved. Fairly good agreement between calculated and found values of the current is found also when the value i_{mean}, at the middle of the section of the catalytic wave between the maximum and minimum, is taken as the value of the limiting catalytic current. As will be seen from Fig. 1 of the previous communication [1], at a potential corresponding to i_{mean}, the wave 1 has almost attained its maximum, whereas the rise in wave 3 has not yet set in, the current being that corresponding to a "pure" catalytic wave.

The value of i_{mean} is readily measured in practice, and it may therefore be used for analytical purposes, whereas for the determination of i_1 it is necessary to obtain the whole polarographic curve and carry out cumbersome calculations. It is thus expedient to take the value i_{mean} as the value of the catalytic current.

Evaluation of the Reaction-rate Constants. From the numerical values of the overall constants we may calculate certain quantities that are involved in them. By use of the values

$$R = 740 \text{ microamp} \cdot \text{liter}^2/\text{mmole}^2 = 740 \text{ amp} \cdot \text{liter}^2/\text{mole}^2 \text{ and } S = 3.38 \cdot 10^{-3} \text{ sq. cm}$$

we obtain

$$k_1 a_B a_{DH^+} = 2.0 \text{ liter}^2/\text{cm}^2 \cdot \text{mole} \cdot \text{sec}$$

For uncharged particles, such as B and BH, we may take a_B as the thickness of the electrode surface layer [9], equal to about $1 \cdot 10^{-10}$ liter/cm^2. The value of a_{DH^+} for hydroxonium ions on the cathode must be greater by a factor of several powers of ten. Its value can be estimated as follows. According to Equations 4 and 6:

$$\overset{\bullet}{a}_{DH^+} = \frac{a_{DH^+}}{1 + b[DH^+]_0} = \frac{[DH^+]_s}{[DH^+]_0}$$

$$a_{DH^+} = [DH^+]_s \frac{1 + b[DH^+]_0}{[DH^+]_0}. \tag{48}$$

When the concentration of acid in the solution is very high and we may assume that the electrode surface is saturated with hydroxonium ions, Equation 48 takes the form:

$$a_{DH^+} = [DH^+]_{s\ \lim} \cdot b. \tag{49}$$

Here, $[DH^+]_{s\ \lim}$ is the limiting surface concentration of hydroxonium ions. If it is assumed that the area occupied by a hydroxonium ion on the electrode surface is about $10\ (\text{Å})^2$, then

$$[DH^+]_{s\ \lim} \simeq 1 \cdot 10^{15} : 6 \cdot 10^{23} \simeq 1.6 \cdot 10^{-9}\ \text{mole/cm}^2$$

and a_{DH^+} is about $5 \cdot 10^{-7}$ liter/cm^2. The value of k_1 is therefore of the order of $4 \cdot 10^{16}$ cm^2/ mole. sec.

The value of the constant k_3 can be obtained from Equation 31.

Using the value $p = 7.8 \cdot 10^4$ microamp^{-1} and assuming that $\kappa_{BH} = \kappa_B = 2.33$ microamp · liter/mmole, we find that $k_3 a_{BH}^2 = 3 \cdot 10^2$ liter^2/cm^2. mole. sec.

If we assume that $a_{BH} = a_B = 1 \cdot 10^{-10}$ liter/cm^2, then the value of k_3 will be of the order of $3 \cdot 10^{22}$ cm^2/ mole. sec.

Thus, the constant for the rate of formation of a hydrogen molecule from complexes of quinine with H atoms is about 10^6 times as great as the rate constant for the interaction of quinine with the hydroxonium ion.

As is shown by the results of our experiments with other proton donors (e.g., NH_4^+) and various catalysts (semicarbazide, pyridine), and also by the results of the authors cited [2, 3, 4], the relation observed between the limiting currents and the composition of the solution is similar in all cases to that found in catalysis with quinine. We may therefore suppose that the hypotheses advanced here are reflections of general laws applying to the catalytic current at a dropping mercury electrode.

I take this opportunity of expressing my great indebtedness to Prof. M. B. Neiman for constant interest in the work.

SUMMARY

1. The previously deduced equations [1] have been verified quantitatively for the catalytic system quinine–hydrochloric acid.

2. The experimental results show that the rate constant for the formation of hydrogen molecules from quinine – hydrogen atom complexes is about 10^6 times as great as the rate constant for the interaction of quinine and hydroxonium ions.

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HETEROGENEOUS EQUILIBRIA IN THE SYSTEMS

$LiCl-RbCl-H_2O$ AND $LiCl-CsCl-H_2O$

V. P. Blidin

There are no data in the literature concerning the solubility relations in aqueous systems containing both lithium chloride (a salt of one of the lightest Group I metals) and rubidium or cesium chloride (salts of the heaviest known alkali metals). The investigation of the chemical interactions of these components in aqueous solutions is of theoretical and practical interest.

It is well known that lithium compounds accompany rubidium and cesium compounds in minerals, soils, and natural waters of various origins, the concentrations of all these compounds being generally quite small. Lithium chloride gives hydrated double salts with many bivalent-metal chlorides: Voskresenskaya and Yanatyeva [1], who studied the system $LiCl-MgCl_2-H_2O$, obtained a salt of composition $LiCl \cdot MgCl_2 \cdot 7H_2O$; Basset and Sandersen [2], investigating the system $LiCl-CoCl-2H_2O$, found several double salts, such as $LiCl \cdot CoCl_2 \cdot 2H_2O$, $7LiCl \cdot 2CoCl_2 \cdot 18H_2O$, and $3LiCl \cdot 2CoCl_2 \cdot 6H_2O$, together with solid solutions over certain concentration ranges; and Benraht [3, 4] showed that LiCl formed similar types of double salts with nickel, manganese, and copper chlorides.

The study of these systems is of interest also because rubidium and cesium chlorides resemble lithium chloride in forming double salts of the same type with salts of the same metals. Thus, in hydrochloric acid solution they form double salts with the chlorides of copper, iron, zinc, cadmium, and manganese. From aqueous solutions containing cobalt chloride, beautiful dark-blue and lilac prismatic crystals separate, and these include the compounds $CoCl_2 \cdot RbCl \cdot 2H_2O$, $CoCl_2 \cdot 2RbCl \cdot 2H_2O$, $CoCl_2 \cdot CsCl \cdot 2H_2O$, $CoCl_2 \cdot 2CsCl \cdot 2H_2O$, $CoCl_2 \cdot 3CsCl \cdot 2H_2O$ [5]. Rubidium and cesium carnallites $RbCl \cdot MgCl_2 \cdot 6H_2O$ and $CsCl \cdot MgCl_2 \cdot 6H_2O$, the analogs of $LiCl \cdot MgCl_2 \cdot 7H_2O$, are found in nature. On the other hand, no hydrated double salts could be detected by Novoselova and Sosnovskaya [6] in the system $LiCl-BeCl_2-H_2O$, nor by Blidin [7] in systems containing lithium chloride together with chlorides of calcium, strontium, and barium.

EXPERIMENTAL

Preparation of the Starting Substances; Methods of Chemical Analysis and Investigation

Lithium chloride was prepared from pure lithium carbonate by dissolving it in chemically pure hydrochloric acid. The dried product was dissolved in alcohol, and the solution was evaporated down on a water bath until crystals of lithium chloride formed. The rubidium and cesium salts were recrystallized and then checked analytically; the results obtained corresponded to chemically pure substances.

Chlorine was determined both gravimetrically and by Mohr titration with 0.01 N $AgNO_3$. Rubidium and cesium were determined as chloroplatinates, the same precipitation conditions being observed as in the determination of potassium. Lithium was determined by difference from the total amount of chlorides.

In order that our results concerning the behavior of the components should be as reliable as possible, we investigated the isotherms at 25° and 40°. The solubility investigations were carried out in an electrically heated water thermostat, in which the temperature was maintained constant within ± 0.1° by means of a toluene thermoregulator. The determination of the solubility of lithium chloride was carried out in a reaction vessel having an oil seal, increasing amounts of rubidium or cesium chloride being added; or alternatively, a saturated solution of the rubidium or cesium salt was taken, and increasing amounts of lithium chloride were added.

The solutions were agitated with a glass stirrer driven by an electric motor. The mixtures were stirred at constant temperature until equilibrium between liquid and solid phases had been established, which generally required 6-8 hours, as indicated by the results of chemical analyses on a number of test samples. After the mixture had settled in the reaction vessel, a sample (0.3-0.5 g) of the liquid phase was removed by pipet and transferred to two weighed weighing bottles. The weighed samples were dissolved in 100 ml measuring flasks, and then separately analyzed for chlorine and rubidium or cesium.

Solid phase was removed in a finely perforated silver spoon, which served as a filter, and the analysis was performed exactly as for the liquid phase. The compositions of the solid phases were determined by the Schreinemakers residue method [8]. The solubility results were plotted on Roozeboom triangles, compositions being expressed in the diagrams in percent by weight.

25° and 40° Isotherms for the System $LiCl - RbCl - H_2O$.

In the investigation of this system, and also of the system $LiCl - CsCl - H_2O$, it was found that as the amount of RbCl (or CsCl) added to a saturated solution of LiCl was increased, the viscosity of the solution increased until the pure components separated out into the solid phase. The analytical data for the isotherms are given in Tables 1 and 2 and represented in the diagrams (Figs. 1 and 2).

The 25° and 40° isotherms have four sections, and there are four solid phases: $LiCl \cdot H_2O$, $RbCl \cdot 2LiCl \cdot 4H_2O$, $3RbCl \cdot LiCl \cdot 2H_2O$ and RbCl.

Thus, our investigations have led to the detection of two types of compounds in this system: $RbCl \cdot 2LiCl \cdot 4H_2O$, and $3RbCl \cdot LiCl \quad 2H_2O$. The compound of the first type, which has a greater solubility than the original components, forms tabular crystals in rosettelike clusters (Fig. 3).

TABLE 1

25° Solubility Isotherms for the System $LiCl - RbCl - H_2O$.

Point No.	Amount (% by wt.)			ε of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	RbCl	H_2O		LiCl	RbCl	
1	45.95	–	54.05	45.95	–	–	$LiCl \cdot H_2O$
2	43.50	6.47	50.03	49.97	54.31	3.62	
3	41.17	11.63	47.20	52.80	52.04	6.70	
4	40.52	15.86	43.62	56.38	–	–	$LiCl \cdot H_2O + RbCl \cdot 2LiCl \cdot 4H_2O$, point B
5	39.05	16.92	44.03	55.97	35.63	28.72	$RbCl \cdot 2LiCl \cdot 4H_2O$
6	33.60	21.86	44.54	55.46	32.20	31.13	
7	30.44	24.17	45.39	54.61	31.26	31.24	
8	29.08	25.21	45.71	54.29	–	–	$RbCl \cdot 2LiCl \cdot 4H_2O + 3RbCl \cdot LiCl \cdot 2H_2O$, point C
9	28.51	21.60	49.89	50.11	17.48	56.03	$3RbCl \cdot LiCl \cdot 2H_2O$
10	26.65	19.52	53.83	46.17	15.64	58.15	
11	23.26	20.04	56.70	43.30	24.13	59.27	
12	19.30	21.48	59.22	40.78	13.07	61.02	
13	12.98	27.45	59.57	40.43	10.10	64.78	
14	8.60	35.09	56.31	43.69	7.84	67.50	
15	6.75	39.87	53.38	46.62	–	–	$3RbCl \cdot LiCl \cdot 2H_2O$ + RbCl, point D
16	5.34	41.55	53.11	46.89	3.25	79.12	RbCl
17	2.60	44.17	53.23	46.77	1.68	81.53	
18	–	48.12	51.88	48.12	–	–	

The compound of the second type $3RbCl \cdot LiCl \cdot 2H_2O$ was similar in external habit to crystals of rhombic syngony (Fig. 4). The compound $RbCl \cdot 2LiCl \cdot 4H_2O$ was less hygroscopic than LiCl; unlike the compound $3RbCl \cdot LiCl \cdot 2H_2O$, which is practically unaffected by a mixture of ether and alcohol, it is decomposed by this mixture.

In order to verify the compositions of the compounds obtained we prepared synthetic solutions corresponding to the compounds, placed these in vessels, and evaporated them isothermally under reduced pressure. The crystals obtained were rapidly pressed between filter papers, and dried in a desiccator over sulfuric acid, the crystals being spread out on a thick layer of filter papers, which gradually imbibed the part of the mother liquor that was not removed by simple pressing. Analysis of the crystals gave the following results:

Found %: RbCl 42.86; LiCl 30.24; H_2O 26.90

$RbCl \cdot 2LiCl \cdot 4H_2O$ Calculated %: RbCl 43.54; LiCl 30.53; H_2O 25.93

Found %: RbCl 81.64; LiCl 9.94; H_2O 8.42

$3RbCl \cdot LiCl \cdot 2H_2O$ Calculated %: RbCl 82.23; LiCl 9.61; H_2O 8.16

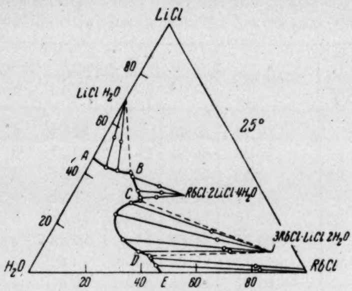

Fig. 1.

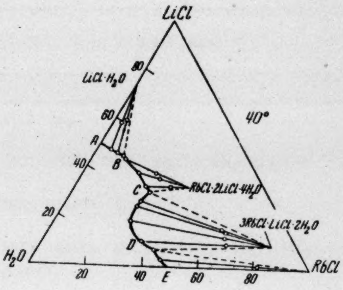

Fig. 2.

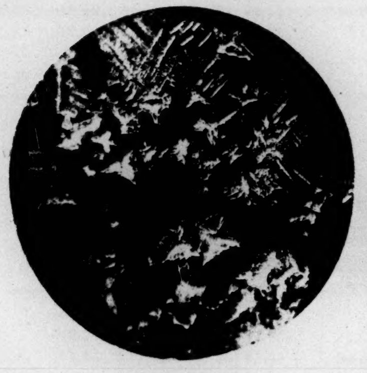

Fig. 3.

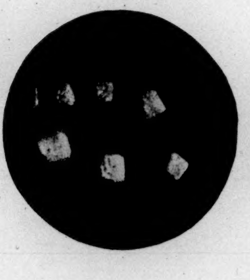

Fig. 4.

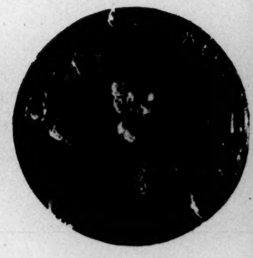

Fig. 7.

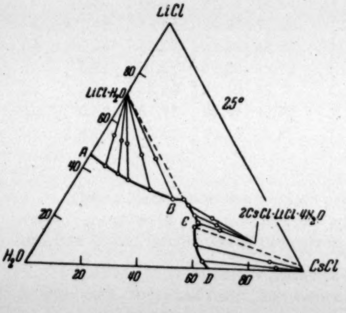

Fig. 5.

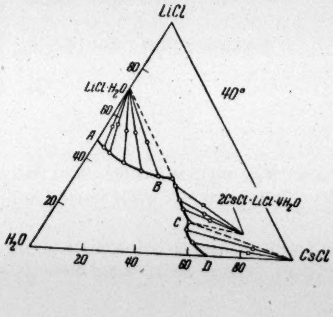

Fig. 6.

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TABLE 2

40° Solubility Isotherms for the System $LiCl-RbCl-H_2O$

Point No.	Amount (% by wt.)			ϵ of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	RbCl	H_2O		LiCl	RbCl	
1	47.98	–	52.02	47.98	–	–	$LiCl \cdot H_2O$
2	46.68	3.47	49.85	50.15	58.72	1.68	
3	45.74	7.26	47.00	53.0	59.53	3.40	
4	45.13	9.51	45.36	54.64	–	–	$LiCl \cdot H_2O + RbCl \cdot 2LiCl \cdot 4H_2O$, point B
5	44.05	10.48	45.47	54.53	39.10	24.38	$RbCl \cdot 2LiCl \cdot 4H_2O$
6	38.02	18.24	43.74	56.26	36.05	27.12	
7	32.51	24.60	42.89	57.11	32.70	32.96	
8	30.22	27.14	42.64	57.36	–	–	$RbCl \cdot 2LiCl \cdot 4H_2O + 3RbCl \cdot LiCl \cdot 2H_2O$, point C
9	26.44	25.46	48.10	51.90	15.86	60.04	$3RbCl \cdot LiCl \cdot 2H_2O$
10	24.43	25.17	50.40	49.60	14.34	62.12	
11	21.26	25.03	53.71	46.29	14.10	63.20	
12	18.45	25.66	55.89	44.11	11.82	63.47	
13	15.50	28.74	55.76	44.24	9.53	65.61	
14	9.78	34.63	55.59	44.41	8.20	65.59	
15	7.34	40.12	52.54	47.46	–	–	$3RbCl \cdot LiCl \cdot 2H_2O + RbCl$, point D
16	2.50	45.26	52.24	47.76	1.50	80.83	RbCl
17	–	49.85	50.15	–	–	–	

TABLE 3

25° Solubility Isotherms for the System $LiCl-CsCl-H_2O$

Point No.	Amount (% by wt.)			ϵ of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	CsCl	H_2O		LiCl	CsCl	
1	45.95	–	54.05	45.95	–	–	$LiCl \cdot H_2O$
2	42.24	5.52	52.24	47.76	55.04	2.46	
3	39.76	11.48	48.76	51.24	53.50	6.14	
4	36.38	16.54	47.02	52.92	52.09	8.97	
5	32.63	26.47	36.90	63.10	74.23	16.12	
6	29.81	36.71	33.48	66.52	46.92	21.50	
7	29.03	40.65	30.32	69.68	–	–	$LiCl \cdot H_2O + 2CsCl \cdot LiCl \cdot 4H_2O$, point B
8	26.38	44.26	29.36	70.64	21.30	55.68	$2CsCl \cdot LiCl \cdot 4H_2O$
9	21.48	47.65	30.87	69.13	17.05	60.03	
10	18.24	49.84	31.92	68.08	15.02	61.48	
11	15.86	51.92	32.22	67.78	–	–	$2CsCl \cdot LiCl \cdot 4H_2O + CsCl$, point C
12	10.12	55.63	34.25	65.75	4.76	84.90	CsCl
13	3.50	61.48	35.02	64.98	1.57	89.07	
14	–	65.51	34.49	65.51	–	–	

The compositions at the multiple points on the isotherms, both in this system and in the $LiCl-CsCl-H_2O$ system, are given in relevant tables (see points B, C, and D). These junction points were determined by interpolation (by the intersection of two curves).

The 25° and 40° solubility isotherms have three sections, and there are three solid phases: $LiCl \cdot H_2O$, $2CsCl \cdot LiCl \cdot 4H_2O$, and CsCl. The compound $2CsCl \cdot LiCl \cdot 4H_2O$, which had a marked monoclinic habit (Fig. 7), was more soluble than its components.

This compound is hygroscopic, though less so than LiCl. It is decomposed by a mixture of ether and alcohol

TABLE 4
40° Solubility Isotherms for the System $LiCl - CsCl - H_2O$.

Point No.	Amount (% by wt.)			ε of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	CsCl	H_2O		LiCl	CsCl	
1	47.98	–	52.02	47.98	–	–	$LiCl \cdot H_2O$
2	46.04	3.91	30.05	49.95	55.53	2.46	
3	43.75	7.46	48.79	51.21	56.86	4.13	
4	40.02	14.63	45.35	54.65	54.42	8.01	
5	37.56	23.34	39.10	70.90	53.68	11.67	
6	35.71	30.12	34.17	65.83	51.06	17.81	
7	33.62	37.05	29.33	70.67	–	–	$LiCl \cdot H_2O + 2CsCl \cdot LiCl \cdot 4H_2O$, point B
8	30.73	39.97	29.30	70.70	23.07	53.48	$2CsCl \cdot LiCl \cdot 4H_2O$
9	24.49	45.83	29.68	70.32	19.93	55.88	
10	19.80	48.65	31.55	68.45	15.81	59.40	
11	15.67	52.24	32.02	67.91	–	–	$CsCl + 2CsCl \cdot LiCl \cdot 4H_2O$, point C
12	12.46	53.68	33.86	66.14	4.61	82.45	CsCl
13	6.50	58.76	34.74	65.26	3.13	81.69	
14	–	67.40	32.60	67.40	–	–	

with separation of fine CsCl crystals. The analytical results for the $2CsCl \cdot LiCl \cdot 4H_2O$ crystals were:

Found %: CsCl 75.16; LiCl 9.52; H_2O 15.32
Calculated %: CsCl 74.64; LiCl 9.39; H_2O 15.96.

It should be noted that as CsCl was added to a saturated solution of LiCl the viscosity of the solution increased, and at the points at which compounds were formed noticeable passage of solid phase into solution occurred.

SUMMARY

1. The 25° and 40° solubility isotherms have been determined for the systems $LiCl - RbCl - H_2O$ and $LiCl - CsCl - H_2O$.

2. The compounds $RbCl \cdot 2LiCl \cdot 4H_2O$ and $3RbCl \cdot LiCl \cdot 2H_2O$ have been found in the first system, and the compound $2CsCl \cdot LiCl \cdot 4H_2O$ has been found in the second system.

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Institute of Hydrochemistry of the USSR Academy of Sciences

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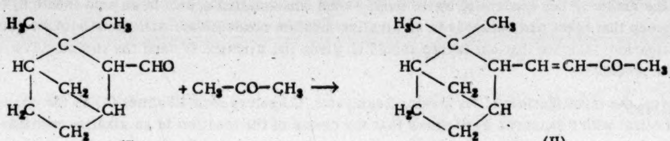
* See Consultants Bureau Translation, page, 893.

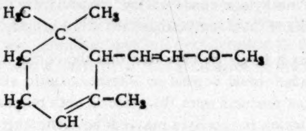
CONDENSATION REACTIONS OF 3-CAMPHENILANECARBOXALDEHYDE WITH KETONES AND ESTERS

B. A. Arbuzov and L. A. Mukhamedova

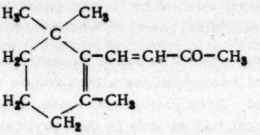
The preparation of 3-camphenilanecarboxaldehyde (I) by the isomerization of camphene oxide [1] has made this aldehyde comparatively accessible for use in various syntheses. In this paper we describe our results on condensation reactions of 3-camphenilanecarboxaldehyde with various ketones, with ethyl acetate, and with ethyl acetoacetate. The condensation product of 3-camphenilanecarboxaldehyde with acetone (II) is an isomer of the α- and β-ionones (III and IIIa):



(I) (II)



(III)



(IIIa)

It differs from them in having an endomethylene bridge, formed at the expense of the disappearance of a double bond. It was of interest to determine the effect of this change of structure on the odor, and with this objective syntheses were carried out of the iosmer of the ionones, the ketone II, and also of a number of its homologs and analogs *.

When 3-camphenilanecarboxaldehyde was condensed with acetone in presence of sodium ethoxide as condensing agent, complete resinification occurred. In presence of aqueous alkali, however, a product having b.p. 139-140° (12 mm); n_D^{20} 1.5030; d_4^{20} 0.9705, was obtained; it had a feeble camphorlike odor. Analysis of this substance gave a low value (by 1%) for carbon, which may be explained by the presence of some of the corresponding aldol.

When, in fact, the product was distilled with camphorsulfonic acid, a substance was obtained which analyzed as $C_{13}H_{20}O$ and had the following constants: b.p. 136-137° (11.5 mm); n_D^{20} 1.5038; d_4^{20} 0.9692; found MR 58.69; calculated for $C_{13}H_{20}O\overline{F}$ MR 57.38, exaltation 1.31. The ketone so obtained (II) was a pale greenish yellow oily liquid having an odor similar to that of ionone. With semicarbazide it yielded a semicarbazone of m.p. 176-177°. The ketone was obtained in 43% yield.

Khusnutdinov gave the following constants for this ketone: b.p. 137-139° (14 mm); n_D^{20} 1.5507; d_4^{20} 0.9721; MR_D 58.20; semicarbazone, m.p. 164-165°. Khusnutdinov's preparation was evidently not free from the aldol.

The condensation of 3-camphenilanecarboxaldehyde with 2-butanone in an alkaline medium went readily, both in presence of aqueous alkali, and in presence of sodium ethylate, the yields of pure product being practically the same in both cases (30% and 33%, respectively). In both cases the same condensation product was obtained and a small amount of the aldol form was present. Distillation of the product over camphorsulfonic acid

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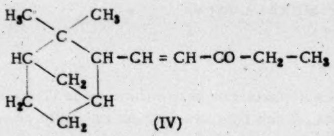
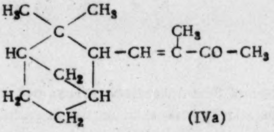
* Similar work was carried out in our laboratory in 1938-1940 by B. Sh. Khusnutdinov. B. Sh. Khusnutdinov was killed in the Great Patriotic War, defending his Fatherland, and he left only a few constants of the compounds he had prepared [2]. The descriptions of the experiments and of the experimental conditions have not been preserved. The work therefore had to be done again.

enabled us to isolate it in the pure state, when it corresponded in composition to $C_{14}H_{22}O$ and had the following constants: b.p. 142-144° (12 mm); n^{20}_{D} 1.5000; d^{20}_{4} 0.9632; Found MR 62.99; Calculated for $C_{14}H_{22}O$ F MR 62.00; exaltation 0.99. The ketone was an oily liquid having an odor similar to that of ionone. Khusnutdinov gave the following constants for this ketone: b.p. 139-140° (12 mm); d^{20}_{4} 0.9608; n^{20}_{D} 1.4980; MR 62.90; semicarbazone, m.p. 200-201°.

The condensation reaction of 3-camphenilanecarboxaldehyde with 2-butanone can give two products (IV and IVa):


(IV)


(IVa)

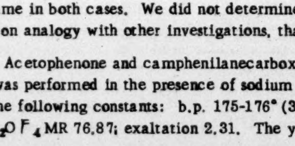
According to the literature [3], the course, of the condensation reaction of aldehydes with acetone homologs depends on the nature of the condensing agent used: when condensation occurs in an acid medium, it is the α-methylene group that takes part, whereas in an alkaline medium condensation will occur with an α-methyl group. These investigations indicate that our ketone should be given the structure IV, and the structure IVa must be regarded as less probable

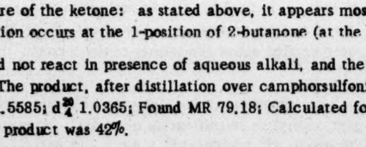
However, the investigations of Nametkin, Isagulyants, Glagoleva, and Kholmer [4] on the course of the condensation of citral with 2-butanone have shown that the course of the reaction in an alkaline medium depends also on whether caustic alkali or sodium alkoxide is used as condensing agent. Condensation in presence of sodium ethoxide occurs in the 1-position, whereas in presence of caustic alkali it occurs in the 3-position of 2-butanone. The two methylionones obtained by "methyl-condensation" and "methylene-condensation" respectively differ inappreciably in physicochemical constants, whereas the melting points of their semicarbazones differ greatly.

By analogy with the results of Nametkin and Isagulyants it might be expected that the course of the condensation reaction of 3-camphenilanecarboxaldehyde with 2-butanone would depend on whether caustic alkali or sodium ethoxide is used. Investigations have shown, however, that our products were the same in both reactions. Their identity was confirmed not only by their physical constants, which in this case may not be sufficiently characteristic, but also by the identity of their semicarbazones: in both cases semicarbazones of m.p. 193-194° were obtained, and in admixture they showed no melting point depression. These results show that the course of the reaction is the same in both cases. We did not determine the structure of the ketone: as stated above, it appears most probable, on analogy with other investigations, that condensation occurs at the 1-position of 2-butanone (at the α-methyl).

Acetophenone and camphenilanecarboxaldehyde did not react in presence of aqueous alkali, and the condensation was performed in the presence of sodium ethoxide. The product, after distillation over camphorsulfonic acid, had the following constants: b.p. 175-176° (3 mm); n^{20}_{D} 1.5585; d^{20}_{4} 1.0365; Found MR 79.18; Calculated for $C_{18}H_{22}O$ F_4 MR 76.87; exaltation 2.31. The yield of pure product was 42%.

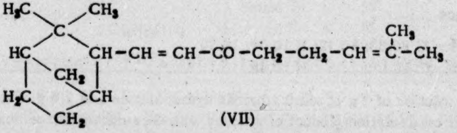
The ketone obtained, 3-(3-camphenilyl)acrylophenone (V), was a viscous greenish-yellow liquid having a feeble spicy odor. Its semicarbazone melted at 167-169°.


(V)

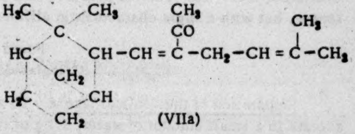

(VI)

3-Camphenilanecarboxaldehyde readily condensed with mesityl oxide in presence of sodium ethoxide. The pure ketone, 1-(3-camphenilyl)-5-methyl-1,4-hexadien-3-one (VI), had the following constants: b.p. 131-133° (1.5 mm); n^{20}_{D} 1.5200; d^{20}_{4} 0.9627; Found MR 73.36; Calculated for $C_{16}H_{24}O$ F_3 MR 70.76; exaltation 2.60. The ketone was a thick oily liquid having a feeble spicy odor.

The condensation of 3-camphenilanecarboxaldehyde with 6-methyl-5-hepten-2-one went very readily in presence of sodium ethoxide. The ketone obtained, after distillation over camphorsulfonic acid, had the following constants: b.p. 166-167° (5 mm); n^{20}_{D} 1.5060; d^{20}_{4} 0.9496; Found MR 81.49; Calculated for $C_{18}H_{28}O$ F_2 MR 80.00; exaltation 1.49. No investigation to determine which of the two possible formulas (VII or VIIa) the ketone possessed was carried out. The ketone was a yellow oily liquid having a feeble spicy odor. The yield of pure product was 37%. The semicarbazone of the ketone melted at 152-153°.



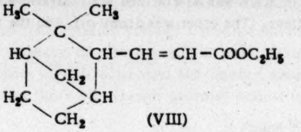
(VII)



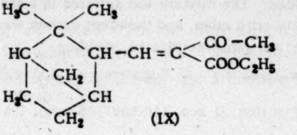
(VIIa)

3-Camphenilanecarboxaldehyde condensed readily with ethyl acetate and with ethyl acetoacetate. The condensation product formed with ethyl acetate (VIII) had the following constants: b.p. 140-142° (10 mm); n$^{20}_{D}$ 1.4890; d$^{20}_{4}$ 0.9893; Found MR 64.85; Calculated for $C_{14}H_{22}O_2$ F MR 63.64; exaltation 1.21. The ester, which was obtained in 51.3% yield, was an oily liquid having a feeble odor.

The condensation of 3-camphenilanecarboxaldehyde with ethyl acetoacetate was carried out in presence of piperidine. The condensation product (IX) had the following constants: b.p. 137-138.5° (2.5 mm); n$^{20}_{D}$ 1.4905; d$^{20}_{4}$ 1.0238; Found MR 74.64; Calculated for $C_{16}H_{24}O_3$ F MR 72.89; exaltation 1.75. The ester IX was a liquid having a feeble pleasant odor. The yield of pure product was 46%.

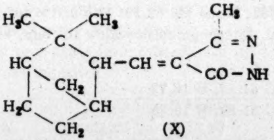


(VIII)



(IX)

When the ethyl ester of α-acetyl-3-camphenilaneacrylic acid (IX) was treated with semicarbazide, a product of m.p. 157-159° was obtained, and this corresponded in its analysis not to the semicarbazone of the keto ester IX, but to the pyrazolone derivative X, which arose by the elimination of a molecule of alcohol from the semicarbazone:



(X)

EXPERIMENTAL

The 3-camphenilanecarboxaldehyde that we used as starting material was obtained by the isomerization of camphene oxide in presence of zinc bromide. In its turn, camphene oxide was prepared by the oxidation of camphene by means of acetylene hydroperoxide in ether solution. The 3-camphenilanecarboxaldehyde boiled at 84° (12 mm) and melted at 65-67°.

Condensation of 3-Camphenilanecarboxaldehyde with Acetone.

To a mixture of 25 g of the aldehyde, 37 g of acetone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The mixture was agitated in a shaker for 32 hours. The mixture was neutralized with tartaric acid and extracted with ether, and the ether extract was dried with calcined sodium sulfate. The ether was drawn off under slightly reduced pressure, and the residue was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fraction I, b.p. 80-127° (12 mm); 10 g; n$^{20}_{D}$ 1.4845

Fraction II, b.p. 127-139° (12 mm); 2.5 g; n$^{20}_{D}$ 1.5000

Fraction III, b.p. 139-140° (12 mm); 13.5 g; n$^{20}_{D}$ 1.5030; d$^{20}_{4}$ 0.9705

Residue, 1 g of resin

Fraction III had a camphorlike odor.

Fractions II and III, after refractionation in presence of a crystal of camphorsulfonic acid, yielded a pure product of b.p. 136-137° (11.5 mm); n_D^{20} 1.5038; d_4^{20} 0.9692; Found MR 58.69; Calculated for $C_{13}H_{20}O$ F MR 57.38; exaltation 1.31. The reaction product was a pale yellowish-green oily liquid having an odor reminiscent of that of ionone, but with a slight characteristic difference.

Found %: C 80.83; 80.72; H 10.39; 10.30

$C_{13}H_{20}O$. Calculated %: C 81.17; H 10.48

Preparation of the Semicarbazone. To a solution of 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate in a small amount of water, 1.7 g of the condensation product of acetone with 3-camphenilanecarboxaldehyde was added, and pure methanol was added to this mixture until solution was complete. The solution was shaken and after 30 minutes the semicarbazone was precipitated, and was filtered off, washed with water, and dried (2.8 g of crude product). After three crystallizations, from ethanol and methanol alternately, the semicarbazone melted at 176-177°. After a fourth crystallization, the melting point did not change.

Found %: N 16.92

$C_{14}H_{23}ON_3$. Calculated %: N 16.86

Condensation of 3-Camphenilanecarboxaldehyde with 2-Butanone

To a mixture of 20 g of the aldehyde, 36 g of 2-butanone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The mixture was agitated in a shaker for 50 hours. The mixture was neutralized with tartaric acid and extracted with ether, and the ether extract was dried with sodium sulfate. The ether was drawn off, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. 90-110° (16 mm); 6.5 g; n_D^{20} 1.4805

Fraction II, b.p. 110-150° (16 mm); 1.4 g; n_D^{20} 1.4890

Fraction III, b.p. 150-155° (16 mm); 10.7 g; n_D^{20} 1.4980

Residue 0.7 g

Fractions II and III were again vacuum-fractionated in presence of camphorsulfonic acid, when drops of water were noted in the condenser. A third fractionation yielded 8.2 g of condensation product having the following constants: b.p. 142-144° (12 mm); n_D^{20} 1.5000; d_4^{20} 0.9632; Found MR 62.99; Calculated for $C_{14}H_{22}O$ F MR 62.00; exaltation 0.99. The reaction product was an oily liquid, faintly greenish yellow in color, and having an odor reminiscent of that of ionone.

Found %: C 81.17; H 10.77

$C_{14}H_{22}O$. Calculated %: C 81.52; H 10.75

The reaction was repeated under different conditions. A solution of 2 g of sodium in 40 ml of ethanol was added to a mixture of 18 g of the aldehyde and 10 g of 2-butanone. The temperature of the reaction mixture rose to 43°, and it became dark red in color. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether extract was dried with sodium sulfate. Ether was drawn off, and the residue was vacuum-fractionated from an Arbuzov flask, yielding

Fraction I, b.p. 89-140° (11.5 mm); 4.5 g

Fraction II, b.p. 140-143.5° (11.5 mm); 3.7 g; n_D^{20} 1.4980

Fraction III, b.p. 143.5-148° (11.5 mm); 7.7 g; n_D^{20} 1.4990

Residue 3.8 g

Fractions II and III were distilled in presence of camphorsulfonic acid and yielded 8 g of the condensation product, which had the following constants: b.p. 140-142° (10.5 mm); n_D^{20} 1.5000; d_4^{20} 0.9630.

Preparation of the Semicarbazone. The substances taken for reaction were 1 g of semicarbazide hydrochloride, 1.5 g of sodium acetate, and 1.8 g of the condensation product of 2-butanone with 3-camphenilanecarboxaldehyde obtained in an aqueous solution of alkali. After 20 minutes the semicarbazone was precipitated (the weight of crude semicarbazone was 2.9g). After four recrystallizations from ethanol and methanol, the semicarbazone melted at 193-194°. A fifth recrystallization did not affect the melting point.

A semicarbazone was prepared also, in a similar way, from the condensation product prepared in presence of sodium ethoxide. It melted at 193-194°, and when the two semicarbazones were mixed the melting point was not depressed.

Found %: N 15.97

$C_{15}H_{25}ON_3$. Calculated %: N 15.95

Condensation of 3-Camphenilanecarboxaldehyde with Acetophenone.

A mixture of 20 g of the aldehyde, 63 g of acetophenone, and 250 ml of water was taken and 40 ml of 2 N caustic soda was added. The reaction mixture was agitated on a shaker for 40 hours, and was then neutralized with tartaric acid and extracted with ether. The ether layer was dried with calcined sodium sulfate, and the ether was then drawn off, and the residue fractionated under reduced pressure. The whole of it came over at 85-87° (12 mm), which corresponds to the boiling point of the original aldehyde and acetophenone.

To the mixture of unchanged starting materials, a solution of 2 g of sodium in 40 ml of ethanol was added, when the temperature rose to 35°. After five minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether layer was dried with calcined sodium sulfate, and, after removal of the ether, the residue was vacuum-fractionated, yielding

Fraction I, b.p. 90-204° (12 mm); 4 g

Fraction II, b.p. 204-210° (12 mm); 17.7 g; n_D^{20} 1.5579.

A second fractionation yielded a product having b.p. 186-188° (6 mm); n_D^{20} 1.5580; d_4^{20} 1.035. This, after fractionation in presence of camphorsulfonic acid, gave a product having the following constants: b.p. 175-176° (3 mm); n_D^{20} 1.5585; d_4^{20} 1.0365; Found MR 79.18; Calculated for $C_{18}H_{22}O\ F_4$ MR 76.87; exaltation 2.31. The reaction product was a thick oily liquid, greenish yellow in color, and having a faint spicy odor.

Found %: C 85.24; H 9.10

$C_{18}H_{22}O$. Calculated %: C 85.04; H 8.72

Preparation of the Semicarbazone. A mixture was prepared from 0.44 g of semicarbazide hydrochloride dissolved in methanol and 0.66 g of sodium acetate dissolved in a small amount of water; 1 g of the condensation product of 3-camphenilanecarboxaldehyde and acetophenone was added, and methanol was added until solution was complete. After five minutes a precipitate of the semicarbazone was obtained, and this was filtered off, washed with water, and dried (weight of crude semicarbazone, 0.7 g). After recrystallization from ethanol, from a mixture of benzene and ethanol, and then again from ethanol, the semicarbazone melted at 167-169°. A fourth recrystallization did not affect the melting point.

Found %: N 13.90

$C_{19}H_{25}ON_3$. Calculated %: N 13.49

Condensation of 3-Camphenilanecarboxaldehyde with Mesityl Oxide.

To a mixture of 20 g of the aldehyde and 15 g of mesityl oxide, a solution of 2 g of sodium in 40 ml of ethanol was added. The temperature rose to 40°. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether; the ether layer was dried with sodium sulfate. The ether was drawn off, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 110° (7 mm); 8 g

Fraction II, b.p. 110-152° (6 mm); 1.2 g; n_D^{20} 1.5150

Fraction III, b.p. 152-156° (5 mm); 15 g; n_D^{20} 1.5180

Residue, 7.2 g of a resinous mass

Fraction III was distilled in presence of camphorsulfonic acid, and then, as a result of a further fractionation, 13 g of a product having the following constants was obtained: b.p. 131-133° (1.5 mm); n_D^{20} 1.5200; d_4^{20} 0.9627; Found MR 73.36; Calculated for $C_{16}H_{24}O\ F_2$ MR 70.76; exaltation 2.60. The condensation product was a yellow oily liquid having a feeble spicy odor.

Found %: C 82.30; H 10.51

$C_{16}H_{24}O$. Calculated %: C 82.70; H 10.41

Condensation of 3-Camphenilanecarboxaldehyde with 6-Methyl-5-hepten-2-one

A solution of 1.5 g of sodium in 35 ml of ethanol was added to a mixture of 15.5 g of the aldehyde and 15 g of 6-methyl-5-hepten-2-one. The temperature rose to 45°, and after three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether extract was dried with sodium sulfate, and, after removal of ether, the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 176° (12 mm); 8 g

Fraction II, b.p. 176-187° (11.5 mm); 3 g; n_D^{20} 1.5043

Fraction III, b.p. 187-189.5° (11.5 mm); 12.3 g n_D^{20} 1.5050

Residue: 4.1 g of resin

Fractions II and III were distilled over camphorsulfonic acid, and refractionation of these fractions then yielded 9.8 g of a product having the following constants: b.p. 166-167° (5 mm); n_D^{20} 1.5060; d_4^{20} 0.9496; Found MR 81.49; Calculated for $C_{18}H_{28}O$ F_2 MR 80.0; exaltation, 1.49. The condensation product was a yellow oily liquid having a spicy odor.

Found %: C 83.37; 83.16; H 11.21; 10.98

$C_{18}H_{28}O$. Calculated %: C 83.01; H 10.84

Preparation of the Semicarbazone. The substances taken for reaction were 0.77 g of semicarbazide hydrochloride, 1.15 g of sodium acetate, and 1.8 g of the condensation product of 3-camphenilanecarboxaldehyde with 6-methyl-5-hepten-2-one. A precipitate appeared after one hour (weight of crude semicarbazide, 2.1 g). After three recrystallizations from benzene and ethanol, the semicarbazone melted at 152-153°. A fourth recrystallization did not affect the melting point.

Found %: N 13.32

$C_{19}H_{31}ON_3$. Calculated %: N 13.23

Condensation of 3-Camphenilanecarboxaldehyde with Ethyl Acetate.

Sodium (6 g) was granulated under a layer of dry toluene, the toluene was poured off, and a mixture, cooled to 0°, of 100 ml of ethyl acetate and 1 ml of absolute alcohol was poured over the sodium. The mixture was cooled with snow and energetically stirred for one hour while a solution of 20 g of 3-camphenilanecarboxaldehyde in 20 ml of ethyl acetate was added dropwise. When the whole of the aldehyde had been added, the reaction mixture was stirred vigorously until the whole of the sodium had reacted. An addition was then made of 18 ml of glacial acetic acid, and the mixture was cautiously diluted with water. The ethyl acetate layer was separated, and the water layer was extracted with ethyl acetate. The united extracts were washed with 120 ml of 6 N hydrochloric acid, and were then washed several times with water and dried with sodium sulfate. The solvent was removed in a water bath, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 125° (11 mm); 1 g

Fraction II, b.p. 125-140° (11 mm); 3 g; n_D^{20} 1.4880

Fraction III, b.p. 140-143° (11 mm); 16.9 g; n_D^{20} 1.4885

Residue: 4.7 g of resin

A second fractionation of Fraction III yielded 15 g of the condensation product, which had the following constants: b.p. 140-142° (10 mm); n_D^{20} 1.4890; d_4^{20} 0.9893; Found MR 64.85; Calculated for $C_{14}H_{22}O_2$ F MR 63.64; exaltation 1.21. It was a greenish-yellow liquid having a faint, pleasant odor.

Found %: C 75.81; H 9.82

$C_{14}H_{22}O_2$. Calculated %: C 75.62; H 9.98

Condensation of 3-Camphenilanecarboxaldehyde with Ethyl Acetoacetate.

A mixture of 20 g of the aldehyde and 17 g of ethyl acetoacetate was cooled to -10-15°, and 1.5 g of piperidine was added. The mixture was set aside in the cold. After 48 hours the reaction mixture was neutralized with dilute sulfuric acid, washed with water, and extracted with ether. The ether layer was dried with sodium sulfate, and the ether was drawn off under reduced pressure. The residue was vacuum-fractionated, and yielded

Fraction I, b.p. to 115° (12.5 mm); 4 g

Fraction II, b.p. 115-168° (12.5 mm); 2.5 g; n_D^{20} 1.4807

Fraction III, b.p. 168-172° (12.5 mm); 17 g; n_D^{20} 1.4882

Residue, 3.3 g

Two fractionations of Fraction III yielded a product (15.9 g) having the following constants: b.p. 137-138.5° (2.5 mm); n_D^{20} 1.4905; d_4^{20} 1.0238; Found MR 74.64; Calculated for $C_{16}H_{24}O_3$ F MR 72.89; exaltation 1.75. It was a colorless liquid of pleasant odor.

Found %: C 72.71; H 9.06

$C_{16}H_{24}O_3$. Calculated %: C 72.69; H 9.15

Preparation of the Semicarbazone. The substances taken for reaction were 0.63 g of semicarbazide hydrochloride, 0.90 g of sodium acetate, and 1.5 g of the condensation product of 3-camphenilanecarboxaldehyde with ethyl acetoacetate. After two hours a precipitate appeared (1 g). Its melting point after two recrystallizations from alcohol was 157-159°.

Found %: N 12.32

$C_{17}H_{27}O_3N_3$. Calculated %: N 13.07

$C_{14}H_{24}ON_3$. Calculated %: N 12.06

SUMMARY

1. 3-Camphenilanecarboxaldehyde has been condensed with acetone, with 2-butanone, with acetophenone, with mesityl oxide, and with 6-methyl-5-hepten-2-one. The products formed from acetone and 2-butanone have odors that are reminiscent of that of ionone, and the products obtained from the other ketones have pleasant feeble spicy odors.

2. 3-Camphenilanecarboxaldehyde has been condensed with ethyl acetate and with ethyl acetoacetate, yielding the corresponding unsaturated esters.

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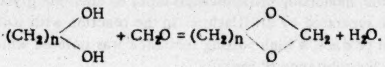
REACTIONS OF BIS(CHLOROMETHYL) ETHERS OF GLYCOLS WITH SODIUM ALKOXIDES

B. A. Arbuzov and G. M. Vinokurova

Alkyl halomethyl ethers have been known for a long time. Bis(chloromethyl) ether was prepared in the middle of the last centry by the chlorination of methanol [1]. In subsequent years some of the alkyl halomethyl ethers attracted the attention of Butlerov [2]. More detailed investigations of halomethyl ethers were made by Tishchenko [3], Henry [4], and Litterscheid and Thimme [5]. The main method used for the preparation of alkyl chloromethyl ethers was by the action of an alcohol and hydrochloric acid on formaldehyde [4].

In 1945 the chloromethylation reaction was used for the preparation of the chloromethyl ethers of various glycols [6, 7]. In the case of glycols the chloromethylation reaction is more complex and is accompanied by the formation of cyclic formals:



The object of the present work was the preparation of new glycol ethers, which have begun to acquire also some practical interest. We have prepared bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol and have studied their reactions with sodium methoxide, ethoxide, isopropoxide, butoxide, and isobutoxide; the 1,2- and 1,3-propanediol ethers were prepared for the first time. The constants of the chloromethyl ethers obtained are given in Table 1.

TABLE 1

Bis(chloromethyl) ether of	B.p. in °C (pressure in mm Hg)	d_4^{20}	n_D^{20}	Yield (%)
Ethylene glycol	102-105 (23)	–	–	60
1,2-Propanediol	87-88 (12)	1.2206	1.4575	44.3
1,3-Propanediol	99-103 (14)	1.2254	1.4600	79.1
1,3-Butanediol	106.5-110 (13)	1.1824	1.4572	21.0
2-Butyne-1,4-diol	150-152 (14)	–	1.4920	55.6

In the chloromethylation of ethyleneglycol, 1,3-propanediol, and 2-butyne-1,4-diol, we obtained only bis(chloromethyl) ethers. In the case of 1,3-butanediol, we obtained also a cyclic formal.

As the work of Lichtenberger and Martin [6] and of Dupont [7] has shown, when sodium ethoxide reacts with chloromethyl ethers of glycols, bis(ethoxymethyl) ethers of glycols are obtained. We have now carried out the reactions of bis(chloromethyl) ethers of glycols with sodium alkoxides in a medium of the corresponding alcohol; the reactions of the bis(chloromethyl) ether of ethylene glycol with sodium butoxide and with sodium isobutoxide were carried out also in an ether medium, in absence of the alcohol. In the case of the bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol treated with sodium methoxide or ethoxide, the reaction proceeded normally, and the corresponding methoxymethyl and ethoxymethyl ethers were obtained in 43-88% yields. The constants of the ethers obtained are given in Table 2.

When the bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol were treated with sodium alkoxides derived from isopropyl and higher alcohols, certain departures from the normal reaction were observed. In most cases, in addition to the normal reaction products, a formal was isolated. In the reactions between the bis(chloromethyl) ether of ethylene glycol and sodium isobutoxide and between the bis(chloromethyl) ether of 1,2-propanediol and sodium butoxide, in addition to the corresponding formals and full ethers of the glycols, products were isolated that corresponded in physicochemical constants and elementary

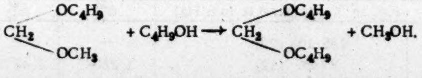
TABLE 2

Bis(alkoxymethyl) ethers of glycols	B. p. in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
$\mathrm{CH_3OCH_2OCH_2CH_2OCH_2OCH_3}$	65-67 (15)	1.4033	1.0027	36.52	36.48	56.61
$\mathrm{CH_3OCH_2OCH_2\overset{CH_3}{\overset{\mid}{C}}HOCH_2OCH_3}$	68-70 (14)	1.4045	0.9814	40.92	41.09	43.63
$\mathrm{C_2H_5OCH_2OCH_2\overset{CH_3}{\overset{\mid}{C}}HOCH_2OC_2H_5}$	87-89 (14)	1.4103	0.9408	50.60	50.33	57.20
$\mathrm{CH_3OCH_2OCH_2CH_2CH_2OCH_2OCH_3}$	62-63.5 (8)	1.4100	0.9946	40.85	40.09	42.95
$\mathrm{C_2H_5OCH_2OCH_2CH_2CH_2OCH_2OC_2H_5}$	98.5-99 (15)	1.4130	0.9470	50.55	50.33	88.33
$\mathrm{CH_3OCH_2O\underset{CH_3}{\underset{\mid}{C}}H-CH_2CH_2OCH_2OCH_2}$	79-80 (12)	1.4120	0.9760	45.39	45.71	64.90
$\mathrm{C_2H_5OCH_2O\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OCH_2OC_2H_5}$	101-102 (14)	1.4148	0.9387	54.93	54.95	72.73
$\mathrm{CH_3OCH_2OCH_2C{\equiv}CCH_2OCH_2OCH_3}$	114-116 (13.5)	1.4417	1.0493	43.85	43.71	89.43

analysis to mono(alkoxymethyl) ethers of glycols. The reactions of the bis(chloromethyl) ether of ethylene glycol with sodium isopropoxide and with sodium butoxide, however, proceeded in quite a different way from the others. In the first reaction it was not found possible to isolate any of the bis(isopropoxymethyl) ether, the products obtained being the formal (diisopropoxymethane), the mono(isopropoxymethyl) ether of ethylene glycol, and a mixture of high-boiling substances which could not be separated by distillation. In the reaction with sodium butoxide, in addition to the formal and the normal reaction product, a high-boiling substance was isolated which corresponded in physicochemical constants and analysis to the substance of formula

$$\mathrm{C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9}.$$

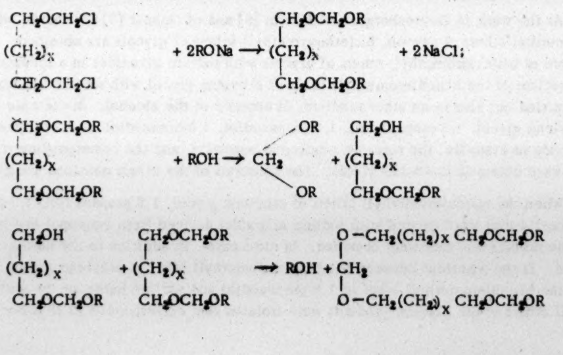
We may suggest, in explanation of the formation of all these anomalous products, that they result from the partial alcoholysis of the normal reaction products, i.e. bis(alkoxymethyl) ethers of glycols. The suggestion of the possibility of the partial alcoholysis of bis(alkoxymethyl) ethers of glycols is confirmed by some investigations of Mamedov carried out in 1942. Mamedov [8] found that dialkoxymethanes undergo alcoholysis, even in an alkaline medium, an alkoxy group of the ether being replaced by the alkoxy group of the alcohol used:



$$\mathrm{\underset{OCH_3}{\overset{OC_4H_9}{CH_2}} + C_4H_9OH \longrightarrow \underset{OC_4H_9}{\overset{OC_4H_9}{CH_2}} + CH_3OH.}$$

However, experiments that we have carried out on the alcoholysis of the bis(butoxymethyl) ether of ethylene glycol, the bis(ethoxymethyl) ether of 1,3-propanediol, and the bis(isobutoxymethyl) ether of 1,3-butanediol in weakly alkaline medium did not give positive results. Guben [9] has also remarked on the high stability of acetals toward alkaline reagents. In weakly acid medium the alcoholysis of glycol ethers goes much more readily and in quantitative yield; this was noted both by Mamedov and by us.

The alcoholysis of bis(alkoxymethyl) ethers of glycols may be represented by the following scheme:



$$\mathrm{\begin{matrix}CH_2OCH_2Cl\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2Cl\end{matrix} + 2RONa \longrightarrow \begin{matrix}CH_2OCH_2OR\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2OR\end{matrix} + 2NaCl;} \tag{1}$$

$$\mathrm{\begin{matrix}CH_2OCH_2OR\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2OR\end{matrix} + ROH \longrightarrow \underset{OR}{\overset{OR}{CH_2}} + \begin{matrix}CH_2OH\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2OR\end{matrix}} \tag{2}$$

$$\mathrm{\begin{matrix}CH_2OH\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2OR\end{matrix} + \begin{matrix}CH_2OCH_2OR\\ \mid\\ (CH_2)_x\\ \mid\\ CH_2OCH_2OR\end{matrix} \longrightarrow ROH + \begin{matrix}O-CH_2(CH_2)_x\,CH_2OCH_2OR\\ \mid\\ CH_2\\ \mid\\ O-CH_2(CH_2)_x\,CH_2OCH_2OR\end{matrix}} \tag{3}$$

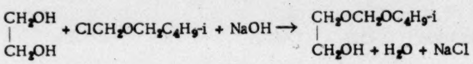
TABLE 3

Reaction Product	B.p. in °C (pressure in mm Hg)		n_D^{20}	d_4^{20}	MR	
					Found	Calculated
$(i\text{-}C_3H_7O)_2CH_2$	117-120		1.3895	0.8206	38.09	37.81
$i\text{-}C_3H_7OCH_2OCH_2CH_2OH$	79-80	(14)	1.4192	0.9771	35.18	34.72
$(n\text{-}C_4H_9O)_2CH_2$	66-67	(13)	1.4068	0.8397	46.88	47.05
$n\text{-}C_4H_9OCH_2OCH_2CH_2$ $\diagdown O$ $n\text{-}C_4H_9OCH_2 \diagup$	132-134	(13)	1.4210	0.9247	64.16	64.18
$C_4H_9OCH_2OCH_2CH_2O$ $\diagdown CH_2$ $C_4H_9OCH_2OCH_2CH_2O \diagup$	183-186	(13)	1.4302	0.9797	81.22	81.32
$(i\text{-}C_4H_9O)_2CH_2$	64	(25)	1.4005	0.8254	47.03	47.05
$i\text{-}C_4H_9OCH_2OCH_2CH_2OH$	89-90.5	(15)	1.4200	0.9492	39.34	39.46
$i\text{-}C_4H_9OCH_2OCH_2$ $\vert$ $i\text{-}C_4H_9OCH_2OCH_2$	124-125	(15)	1.4173	0.9185	64.47	64.18
$i\text{-}C_3H_7OCH_2OCH_2$ $\vert$ $i\text{-}C_3H_7OCH_2OCH-CH_3$	101-102	(12)	1.4130	0.9170	59.82	59.57
$C_4H_9OCH_2OCH_2CHOH$ $\vert$ CH_3	85-86	(9)	1.4250	0.9401	44.08	43.95
$C_4H_9OCH_2OCH_2CHOCH_2OC_4H_9$ $\vert$ CH_3	142-143	(15)	1.4240	0.9131	69.27	68.80
$i\text{-}C_4H_9OCH_2OCH_2$ $\vert$ $i\text{-}C_4H_9OCH_2OCH-CH_3$	129-131	(14)	1.4190	0.9062	68.97	68.80
$i\text{-}C_3H_7OCH_2OCH_2 \diagdown$ CH_2 $i\text{-}C_3H_7OCH_2OCH_2 \diagup$	106-109	(13)	1.4160	0.9220	59.87	59.57
$C_4H_9OCH_2OCH_2 \diagdown$ CH_2 $C_4H_9OCH_2OCH_2 \diagup$	136-138	(9)	1.4255	0.9199	69.00	68.81
$i\text{-}C_4H_9OCH_2OCH_2 \diagdown$ CH_2 $i\text{-}C_4H_9OCH_2OCH_2 \diagup$	120-123	(8)	1.4225	0.9117	69.19	68.81
$\diagup CH_3$ $i\text{-}C_3H_7OCH_2OCH \diagdown$ CH_2 $i\text{-}C_3H_7OCH_2OCH_2 \diagup$	113-116	(11)	1.4170	0.9159	64.25	64.18
$\diagup CH_3$ $C_4H_9OCH_2OCH \diagdown$ CH_2 $C_4H_9OCH_2OCH_2 \diagup$	152-154	(15)	1.4260	0.9163	73.26	73.42
$\diagup CH_3$ $i\text{-}C_4H_9OCH_2OCH \diagdown$ CH_2 $i\text{-}C_4H_9OCH_2OCH_2 \diagup$	130-131.5	(8.5)	1 4235	0.9064	73.68	73.42
$i\text{-}C_3H_7OCH_2OCH_2C$ $\vert\vert\vert$ $i\text{-}C_3H_7OCH_2OCH_2C$	138-140	(13.5)	1.4398	0.9748	62.16	62.18
$C_4H_9OCH_2OCH_2C$ $\vert\vert\vert$ $C_4H_9OCH_2OCH_2C$	155-158	(6)	1.4437	0.9574	71.53	71.39
$i\text{-}C_4H_9OCH_2OCH_2C$ $\vert\vert\vert$ $i\text{-}C_4H_9OCH_2OCH_2C$	145	(6)	1.4400	0.9506	71.53	71.39

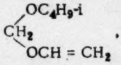
In this way the formation of all the by-products can be explained. The constants of the ethers obtained are shown in Table 3.

It should be noted that all of the substances given in the table, with the exception of diisopropoxy-, dibutoxy- and diisobutoxy-methanes and the bis(butoxymethyl) ether of ethylene glycol, were prepared for the first time; the constants of the compounds that have been prepared previously were completely in accord with the values obtained by Mamedov.

However, a number of our results do not agree with those of Mamedov. In carrying out the synthesis of the mono(isobutoxymethyl) ester of ethylene glycol according to the equation



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + ClCH_2OCH_2C_4H_9\text{-}i + NaOH \rightarrow \begin{array}{l} CH_2OCH_2OC_4H_9\text{-}i \\ | \\ CH_2OH + H_2O + NaCl \end{array}$$

Mamedov obtained two fractions. He considered the first fraction b.p. 80-88°[11 mm]; d^{20}_{20} 0.8399; n^{20}_{D} 1.4047 to be the product of the dehydration of the hydroxy ether  $CH_2(OC_4H_9\text{-}i)(OCH=CH_2)$, and in support of his contention Mamedov cited molecular-weight determinations (cryoscopical in benzene), double-bond estimation, and elementary analysis:

Found %: Br_2 0.2308; C 63.77; H 11.47; M 138.3
Calculated %: Br_2 0.2123; C 64.71; H 10.77; M 130

He regarded the second fraction b.p. 110-118° [5 mm]; d^{20}_{20} 0.9188; n^{20}_{D} 1.4165 as the mono(isobutoxymethyl) ether of ethylene glycol: Found M 150.37; MR 40.59; Calculated M 148; MR 39.33;

Found %: OH 12.3; C 56.75; H 11.59
Calculated %: OH 11.48; C 57.00; H 10.8

In the reaction between the bis(chloromethyl) ether of ethylene glycol and sodium isobutoxide we also obtained two products, their constants being:

1. B.p. 89-90.5° (15 mm); n^{20}_{D} 1.4200; d^{20}_{4} 0.9492; Found MR 39.34; Calculated for $C_7H_{16}O_3$ MR 39.46

Found %: C 56.40; H 10.47
Calculated %: C 56.75; H 10.81

2. B.p. 124-125° (15 mm); n^{20}_{D} 1.4173; d^{20}_{4} 0.9185; Found MR 64.47; Calculated for $C_{12}H_{26}O_4$ MR 64.18

Found %: C 61.29; H 11.32
Calculated %: C 61.53; H 11.11

By reference to the molecular refraction and elementary analysis we established that the product of b.p. 89-90.5° (15 mm) was the mono(isobutoxymethyl) ether of ethylene glycol, and the product of b.p. 124-125° (15 mm) was the bis(isobutoxymethyl) ether of ethylene glycol. Thus a comparison of our results with those of Mamedov shows that products having similar physical constants have been taken to be two different compounds, and the constants of our mono(isobutoxymethyl) ether of ethylene glycol and Mamedov's mono(isobutoxymethyl) ether of ethylene glycol do not correspond with each other.

A study of our results and those of Mamedov concerning the products of b.p. 110-118° (5 mm) and 124-125° (15 mm) forces one to the conclusion that we are dealing here with one and the same bis(isobutoxymethyl) ether of ethylene glycol, the only difference being that Mamedov's product was impure. In fact, the wide boiling range (8°) of Mamedov's product, and consequently the large discrepancy between theoretical and practical values of the molecular refraction, and also the analytical data — all these confirm this suggestion. The only perplexing point is Mamedov's analysis for hydroxyl. The cause of the difference in the experimental results obtained in our work and in that of Mamedov can be determined only by a verification of Mamedov's results [10].

EXPERIMENTAL

Preparation of the Bis(chloromethyl) Ether of 1,2-Propanediol

The bis(chloromethyl) ether of 1,2-propanediol was prepared by the chloromethylation of 1,2-propanediol by the method developed by Lichtenberger and Martin, and also by Dupont and coworkers [6, 7]. A mixture of 200 g of 1,2-propanediol and 155.8 g of powdered paraformaldehyde was introduced into a round-bottomed flask surrounded with a cooling mixture, and was stirred carefully. A stream of dry hydrogen chloride was passed through the mixture until full saturation was attained. After 5-6 hours, two layers formed. The upper, water layer was poured off, and the lower layer was dried with calcium chloride and fractionated from an Arbuzov flask. The fractionation yielded the bis(chloromethyl) ether of 1,2-propanediol, yield 44-45%; b.p. 87-88° (12 mm); d_4^{20} 1.2195; n_D^{20} 1.4592; Found MR 39.03; Calculated for $C_5H_{10}O_2Cl_2$ MR 39.41.

Found %: Cl 41.20

$C_5H_{10}O_2Cl_2$. Calculated %: Cl 41.04

The bis(chloromethyl) ether of 1,2-propanediol is a clear liquid that fumes in air and has a sharp odor and lachrymatory properties.

Preparation of the Bis(chloromethyl) Ether of 1,3-Propanediol

The bis(chloromethyl) ether of 1,3-propanediol was prepared similarly to all of the other such glycol ethers. A current of dry hydrogen chloride was passed through a mixture of 145.5 g of 1,3-propanediol and 114.5 g of paraformaldehyde. When saturation was complete, the two layers formed were separated. The lower layer, an oily liquid, was dried with calcium chloride and fractionated from an Arbuzov flask. Two fractionations yielded the required ether in 79.10% yield; it had b.p. 99-103: (12 mm); d_4^{20} 1.2254; n_D^{20} 1.4600; Found MR 38.67; Calculated for $C_5H_{10}O_2Cl_2$ MR 38.31

Found %: Cl 41.24

$C_5H_{10}O_2Cl_2$. Calculated %: Cl 41.04

The bis(chloromethyl) ether of 1,3-propanediol is a heavy liquid that fumes lightly in air and has a sharp odor and somewhat lachrymatory properties.

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

A solution of sodium methoxide was prepared in a 500-ml round-bottomed flask, fitted with reflux condenser and dropping funnel, by addition of 11.5 g of sodium to 200 ml of absolute methanol, and was cooled to about room temperature. To the constantly stirred solution, 50 g of the bis(chloromethyl) ether of ethylene glycol was then added dropwise, when a precipitate of sodium chloride immediately appeared and the reaction mixture became warm. Reaction was completed by heating of the mixture in a water bath for one hour. The sodium chloride was filtered off, and the filtrate was fractionated from a flask provided with a Widmer column. The fractionation gave a 56.61% yield of the bis(methoxymethyl) ether of ethylene glycol, b.p. 65-67° (15 mm); d_4^{20} 1.0027; n_D^{20} 1.4033; Found MR 36.52; Calculated for $C_6H_{14}O_4$ MR 36.48

Found %: C 47.96; H 9.10

$C_6H_{14}O_4$. Calculated %: C 48.00; H 9.33

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

The bis(chloromethyl) ether of ethylene glycol (30 g) was added dropwise with shaking of the flask to a solution of sodium isopropoxide prepared from 8.6 g of sodium and 300 ml of absolute isopropyl alcohol. The procedure was similar to that of the preceding experiment, heating in the water bath being for one hour. Repeated fractionation yielded:

1. Diisopropoxymethane in 24.49% yield, b.p. 117-120°; d_4^{20} 0.8206; n_D^{20} 1.3895; Found MR 38.09; Calculated for $C_7H_{16}O_2$ MR 37.81. Mamedov found b.p. 118-119°; n_D^{20} 1.3865; d_4^{20} 0.8197.

2. The mono(isopropoxymethyl) ether of ethylene glycol, b.p. 79-80° (14 mm); d_4^{20} 0.9771; n_D^{20} 1.4194; Found MR 35.18; Calculated for $C_6H_{14}O_3$ MR 34.72.

Found %: C 53.38; H 10.40

$C_6H_{14}O_3$. Calculated %: C 53.73; H 10.44

3. A mixture of high-boiling products, which it was not found possible to fractionate.

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

Experiment 1. The bis(chloromethyl) ether of ethylene glycol (30 g) was added dropwise to a constantly shaken solution of sodium butoxide prepared from 8.6 g of sodium and 220 ml of absolute butyl alcohol. The mixture was heated in an oil bath for 90 minutes. Fractionation yielded dibutoxymethane in 87.70% yield; it had b.p. 66-67° (13 mm); d_4^{20} 0.8397; n_D^{20} 1.4068; Found MR 46.88; Calculated for $C_9H_{20}O_2$ MR 47.05

Found %: C 67.19; H 12.49

$C_9H_{20}O_2$. Calculated %: C 67.5; H 12.5

Experiment 2. The reaction between sodium butoxide and the bis(chloromethyl) ether of ethylene glycol was repeated under somewhat different conditions. The alkoxide was prepared by the swelling method [11], and the reaction was carried out in an ether medium, as follows. The bis(chloromethyl) ether of ethylene glycol (45 g) was added dropwise to 53 g of sodium butoxide in absolute ether, when the reaction flask became somewhat warm. When addition of the chloro ether was complete, the reaction was continued by heating the mixture in a water bath for ten hours. Even after this prolonged heating, however, reaction was not complete. In order to free the mixture from the bis(chloromethyl) ether of ethylene glycol, which would have inevitably interfered in the fractionation, the contents of the flask were treated with water, the reaction product was extracted with ether, and the ether extract was dried with calcium chloride and then fractionated, yielding:

1. Dibutoxymethane in 34.73% yield; it had b.p. 65-69.5° (15 mm); d_4^{20} 0.8378; n_D^{20} 1.4090; Found MR 47.24; Calculated for $C_9H_{20}O_2$ MR 47.05.

2. The bis(butoxymethyl) ether of ethylene glycol, b.p. 132-134° (13 mm); d_4^{20} 0.9247; n_D^{20} 1.4210; Found MR 64.16; Calculated for $C_{12}H_{26}O_4$ MR 64.18; yield 17.22%;

Found %: C 61.29; H 11.02
$C_{12}H_{26}O_4$. Calculated %: C 61.53; H 11.11

3. $C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$ in 5.86% yield; it had the following constants: b.p. 183-186° (13 mm); d_4^{20} 0.9797; n_D^{20} 1.4302; Found MR 81.22; Calculated for $C_{15}H_{32}O_6$. MR 81.32.

Found %: C 58.37; H 10.22
$C_{15}H_{32}O_6$. Calculated %: C 58.44; H 10.38

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

Experiment 1. The reaction was carried out in the usual way. The bis(chloromethyl) ether of ethylene glycol (50 g) was added to a solution of sodium isobutoxide prepared from 14.4 g of sodium and 200 ml of absolute isobutyl alcohol, and the reaction was completed by heating the mixture in an oil bath for three hours. Fractionation of the reaction products yielded:

1. Diisobutoxymethane in 70.15% yield; it had b.p. 63-64° (25 mm); d_4^{20} 0.8254; n_D^{20} 1.4005; Found MR 47.03; Calculated for $C_9H_{20}O_2$ MR 47.05.

Found %: C 66.99; H 12.15
$C_9H_{20}O_2$. Calculated %: C 67.5; H 12.5

The literature gives b.p. 164.3° and n_D^{20} 1.4020 [12].

2. The mono(isobutoxymethyl) ether of ethylene glycol (7.7 g), b.p. 89-90.5° (15 mm); d_4^{20} 0.9492; n_D^{20} 1.4200; Found MR 39.34; Calculated for $C_7H_{16}O_3$ MR 39.46.

Found %: C 56.40; H 10.47
$C_7H_{16}O_3$. Calculated %: C 56.75; H 10.81

3. The bis(isobutoxymethyl) ether of ethylene glycol (7.2 g), b.p. 124-125° (15 mm); d_4^{20} 0.9185; n_D^{20} 1.4173; Found MR 64.47; Calculated for $C_{12}H_{26}O_4$ MR 64.18.

Found %: C 61.29; H 11.32
$C_{12}H_{26}O_4$. Calculated %: C 61.53; H 11.11

Experiment 2. The reaction between sodium isobutoxide and the bis(chloromethyl) ether of ethylene glycol was repeated under different conditions. The alkoxide was prepared by the swelling method. To 53 g of sodium isobutoxide in ether, 50 g of the bis(chloromethyl) ether of ethylene glycol was added dropwise, and when the whole of the chloro ether had been added, the reaction flask was heated in a water bath for ten hours. However, in this case also reaction did not go to completion. In order, therefore, to hydrolyze unchanged chloro ether, the contents of the flask were treated with water, and the reaction products were extracted with ether. The ether extract was dried with calcium chloride, the ether was driven off, and the residue was fractionally distilled from a flask having a Widmer column. The products were: 19.8 g of diisobutoxymethane, b.p. 59-64° at 21 mm; n_D^{20} 1.4010 (the literature gives b.p. 164.3°; n_D^{20} 1.4020 [12]) and 8 g of the bis(isobutoxymethyl) ether of ethylene glycol, b.p. 119-121° (12 mm); d_4^{20} 0.9160; n_D^{20} 1.4179; Found MR 64.37; Calculated for $C_{12}H_{26}O_4$ MR 64.18. It was not found possible to isolate any pure substance by fractionation of the high-boiling fraction.

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 10.2 g of sodium, 200 ml of absolute methanol, and 30 g of the bis(chloromethyl) ether of 1,2-propanediol. The mixture was heated in the water bath for one hour. The bis(methoxymethyl) ether of 1,2-propanediol was isolated in 43.63% yield; it had b.p. 68-70° (14 mm); d_4^{20} 0.9814; n_D^{20} 1.4045; Found MR 40.92; Calculated for $C_7H_{16}O_4$ MR 41.09.

Found %: C 51.31; H 9.94
$C_7H_{16}O_4$. Calculated %: C 51.22; H 9.75

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The bis(chloromethyl) ether of 1,2-propanediol (20 g) was added dropwise to a solution of 15.7 g of sodium ethoxide in 250 ml of absolute alcohol, and the mixture was heated in a water bath for one hour. The bis(ethoxymethyl) ether of 1,2-propanediol was isolated in 57.20% yield; it had b.p. 87-89° (14 mm); d_4^{20} 0.9408; n_D^{20} 1.4103; Found MR 50.60; Calculated for $C_9H_{20}O_4$ MR 50.33.

Found %: C 56.10; H 10.52
$C_9H_{20}O_4$. Calculated %: C 56.25; H 10.41

The ether so obtained is a clear liquid having a pleasant feeble odor.

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 15 g of the bis(chloromethyl) ether of 1,2-propanediol and 14.2 g of sodium isopropoxide. The mixture was heated in a water bath for one hour. The bis(isopropoxymethyl) ether of 1,2-propanediol was isolated in 54.73% yield; it had b.p. 101-102° (12 mm); d_4^{20} 0.9170; n_D^{20} 1.4130; Found MR 59.82; Calculated for $C_{11}H_{24}O_4$ MR 59.57.

Found %: C 59.63; H 10.83
$C_{11}H_{24}O_4$. Calculated %: C 60.00; H 10.90

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 30 g of the bis(chloromethyl) ether of 1,2-propanediol and 33.3 g of sodium butoxide. The mixture was heated in an oil bath for one hour. As a result of the reaction, three substances were obtained:

1. Dibutoxymethane (10.3 g), b.p. 47-48° at 4 mm; d_4^{20} 0.8378; n_D^{20} 1.4090; Found MR 47.24; Calculated for $C_9H_{20}O_2$ MR 47.05.

2. The mono(butoxymethyl) ether of 1,2-propanediol, b.p. 85-86° (9 mm); d_4^{20} 0.9401; n_D^{20} 1.4250; Found MR 44.08; Calculated for $C_8H_{18}O_3$ MR 43.95. (7 g).

Found %: C 59.33; H 11.23
$C_8H_{18}O_3$. Calculated %: C 59.25; H 11.11

3. The bis(butoxymethyl) ether of 1,2-propanediol,(14 g), b.p. 142-143° (15 mm); d_4^{20} 0.9131; n_D^{20} 1.4240; Found MR 69.27; Calculated for $C_{13}H_{28}O_4$ MR 68.80.

Found %: C 62.68; H 11.24
$C_{13}H_{28}O_4$. Calculated %: C 62.9; H 11.29

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The procedure was similar to that of the reactions described above. The reactants were 20 g of the bis(chloromethyl) ether of 1,2-propanediol and 22.19 g of sodium isobutoxide, and the mixture was heated in an oil bath for one hour. The products isolated were 9 g of diisobutoxymethane, b.p. 48-52° at 13 mm; n_D^{20} 1.4020; and 12.2 g of the bis(isobutoxymethyl) ether of 1,2-propanediol, b.p. 127-128° at 14 mm; d_4^{20} 0.9062; n_D^{20} 1.4190; Found MR 68.97; Calculated for $C_{13}H_{28}O_4$ MR 68.80.

Found %: C 62.80; H 11.04
$C_{13}H_{28}O_4$. Calculated %: C 62.90; H 11.29

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure was similar to that of the preceding reactions. The chloro ether (30 g) was added dropwise to a solution of 18.7 g of sodium methoxide in 200 ml of absolute methanol. Heating was continued for 30 minutes. The product was 12.2 g of the bis(methoxymethyl) ether of 1,3-propanediol, b.p. 79° (16 mm); d_4^{20} 0.9946; n_D^{20} 1.4100; Found MR 40.85; Calculated for $C_7H_{16}O_4$. MR 41.09.

Found %: C 50.96; H 9.85
$C_7H_{16}O_4$. Calculated %: C 51.22; H 9.75

In addition, 3.5 g of 1,3-propanediol was obtained, it had b.p. 98-100° at 8 mm; d^{20}_{4} 1.049; n^{20}_{D} 1.4370; Found MR 18.91; Calculated for $C_3H_8O_2$ MR 19.10.

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The bis(chloromethyl) ether of 1,3-propanediol (20 g) was added dropwise to a solution of 15.72 g of sodium ethoxide in 300 ml of absolute ethanol, and the mixture was heated in a water bath for 90 minutes. Sodium chloride was filtered off, and the filtrate was vacuum-fractionated, yielding the bis(ethoxymethyl) ether of 1,3-propanediol in 88.33% yield; it had b.p. 97-98.5° (14 mm); d^{20}_{4} 0.9470; n^{20}_{D} 1.4130; Found MR 50.55; Calculated for $C_9H_{20}O_4$ MR 50.33.

Found %: C 56.13; H 10.54
$C_9H_{20}O_4$ Calculated %: C 56.25; H 10.41

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

To 18.9 g of sodium isopropoxide, 20 g of the bis(chloromethyl) ether of 1,3-propanediol was added dropwise, and the mixture was heated in a water bath for one hour. Sodium chloride was filtered off, and the filtrate was fractionally distilled from a flask fitted with a Widmer column. The bis(isopropoxymethyl) ether of 1,3-propanediol was obtained in 70% yield; it had b.p. 106-109° (13 mm); d^{20}_{4} 0.9220; n^{20}_{4} 1.4160; Found MR 59.87; Calculated for $C_{11}H_{24}O_4$ MR 59.57.

Found %: C 59.67; H 10.87
$C_{11}H_{24}O_4$ Calculated %: C 60.00; H 10.90

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure followed that of the preceding reactions, 22.19 g of sodium butoxide, 350 ml of absolute butyl alcohol, and 20 g of the bis(chloromethyl) ether of 1,3-propanediol being taken. The products obtained were dibutoxymethane in 37.85% yield, b.p. 58° (8 mm); n^{20}_{D} 1.4090; and the bis(butoxymethyl) ether of 1,3-propanediol in 55.24% yield, b.p. 136-138° (9 mm); d^{20}_{4} 0.9199; n^{20}_{D} 1.4255; Found MR 69.00; Calculated for $C_{13}H_{28}O_4$ MR 68.81.

Found %: C 63.17; H 11.25
$C_{13}H_{28}O_4$ Calculated %: C 62.90; H 11.29

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure followed that of the preceding reactions, the reactants being 15 g of the bis(chloromethyl) ether of 1,3-propanediol and 16.6 g of sodium isobutoxide in 250 ml of absolute isobutyl alcohol. The products isolated were 4.7 g of diisobutoxymethane, b.p. 160-161°; n^{20}_{4} 1.4010; and 13.7 g of the bis(isobutoxymethyl) ether of 1,3-propanediol, b.p. 120-123° at 8 mm; d^{20}_{4} 0.9117; n^{20}_{D} 1.4225; Found MR 69.19; Calculated for $C_{13}H_{28}O_4$ MR 68.81.

Found %: C 62.87; H 11.07
$C_{13}H_{28}O_4$ Calculated %: C 62.90; H 11.29

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reaction was carried out in a round-bottomed flask fitted with dropping funnel and reflux condenser. The bis(chloromethyl) ether of 1,3-butanediol (30 g) was added dropwise to 17.3 g of sodium methoxide in 200 ml of absolute methanol. The reaction was completed by heating the mixture in a water bath for one hour. The bis(methoxymethyl) ether of 1,3-butanediol was isolated in 64.9% yield; it had b.p. 79-80° (12 mm); d^{20}_{4} 0.9760; n^{20}_{D} 1.4120; Found MR 45.39; Calculated for $C_8H_{18}O_4$ MR 45.71.

Found %: C 53.95; H 10.29
$C_8H_{18}O_4$ Calculated %: C 53.93; H 10.11

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reactants were 14.54 g of sodium ethoxide in 300 ml of absolute ethanol and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The bis(ethoxymethyl) ether of 1,3-butanediol was obtained in 45.4% yield; it had b.p. 101-102° (14 mm); d^{20}_{4} 0.9387; n^{20}_{D} 1.4148; Found MR 54.93; Calculated for $C_{10}H_{22}O_4$ MR 54.95.

Found %: C 57.91; H 10.39
$C_{10}H_{22}O_4$ Calculated %: C 58.25; H 10.67

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

To a solution of 17.54 g of sodium isopropoxide in 250 ml of absolute isopropyl alcohol, 20 g of the bis(chloromethyl) ether of 1,3-butanediol was added dropwise. The product isolated was 13.9 g of the bis(isopropoxymethl) ether of 1,3-butanediol, b.p. 113-116° (11 mm); d_4^{20} 0.9159; n_D^{20} 1.4170; Found MR 64.25; Calculated for $C_{12}H_{26}O_4$ MR 64.18.

Found %: C 61.43; H 11.10
$C_{12}H_{26}O_4$ Calculated %: C 61.53; H 11.11

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The procedure was similar to that of the preceding reactions, the reactants being 20.5 g of sodium butoxide, in 250 ml of absolute butyl alcohol and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The products isolated were 10.2 g of dibutoxymethane, b.p. 74.5-75.5° (17 mm); n_D^{20} 1.4085; and 9 g of the bis(butoxymethyl) ether of 1,3-butanediol, b.p. 152-154° (15 mm); d_4^{20} 0.9163; n_D^{20} 1.4260; Found MR 73.26; Calculated at $C_{14}H_{30}O_4$ MR 73.42.

Found %: C 63.81; H 11.22
$C_{13}H_{30}O_4$ Calculated %: C 64.12; H 11.45

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reaction was carried out as usual, the reactants being 20.5 g of sodium isobutoxide and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The products isolated were 4.5 g of diisobutoxymethane, b.p. 160°; n_D^{20} 1.4030; and 20.2 g of the bis(isobutoxymethyl) ether of 1,3-butanediol, b.p. 130-131.5° (8.5 mm); d_4^{20} 0.9064; n_D^{20} 1.4235; Found MR 73.68; Calculated for $C_{14}H_{30}O_4$ MR 73.42.

Found %: C 63.99; H 11.35
$C_{14}H_{30}O_4$ Calculated %: C 64.12; H 11.45

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reaction was carried out as usual, the reactants being 8.85 g of sodium methoxide in 150 ml of absolute methanol and 15 g of the bis(chloromethyl) ether of 2-butyne-1,4-diol. The bis(methoxymethyl) ether of 2-butyne-1,4-diol was obtained in 89.43% yield; it had b.p. 114-116° (11 mm); d_4^{20} 1.0493; n_D^{20} 1.4417; Found MR 43.85; Calculated for $C_8H_{14}O_4 \,|\!\equiv$ MR 43.71.

Found %: C 54.64; H 7.76
$C_8H_{14}O_4$ Calculated %: C 55.17; H 8.04

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reactants were 13.4 g of sodium isopropoxide in 200 ml of absolute isopropyl alcohol and 15 g of the bis(chloromethyl) ether in 2-butyne-1,4-diol. The product isolated was 7.3 g of the required bis(isopropoxymethyl) ether of 2-butyne-1,4-diol, b.p. 138-140° (13.5 mm); d_4^{20} 0.9748; n_D^{20} 1.4398; Found MR 62.16; Calculated for $C_{12}H_{22}O_4 \,|\!\equiv$ MR 62.18.

Found %: C 61.99; H 9.45
$C_{12}H_{22}O_4$ Calculated %: C 62.17; H 9.56

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reactants were 15.7 g of sodium butoxide in 200 ml of absolute butyl alcohol and 15 g of the chloro ether. It was found possible, after several fractionations, to isolate 1.7 g of dibutoxymethane, b.p. 55-58° (6 mm); and 13.2 g of the bis(butoxymethyl) ether of 2-butyne-1,4-diol, b.p. 155-158° (6 mm); d_4^{20} 0.9574; n_D^{20} 1.4437; Found MR 71.53; Calculated for $C_{14}H_{26}O_4 \,|\!\equiv$ MR 71.39.

Found %: C 64.87; H 9.89
$C_{14}H_{26}O_4$ Calculated %: C 65.11; H 10.00

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The chloro ether (15 g) was added dropwise to a solution of 15.7 g of sodium isobutoxide in 200 ml of absolute isobutyl alcohol. The products isolated were 2 g of diisobutylmethane, b.p. 159-161°; n_D^{20} 1.4005; and 17.7 g of the bis(isobutoxymethyl) ether of 2-butyne-1,4-diol, b.p. 145° (6 mm); d_4^{20} 0.9506; n_D^{20} 1.4400; Found MR 71.53; calculated at $C_{14}H_{26}O_4 \,|\!\equiv$ MR 71.39.

Found %: C 65.36; H 9.68
$C_{14}H_{26}O_4$ Calculated %: C 65.11; H 10.04

Alcoholysis of the Bis(ethoxymethyl) Ether of 1,3-Propanediol

A solution of sodium ethoxide obtained by dissolving 0.1 g of sodium in 40 ml of absolute ethanol was introduced into a round-bottomed flask fitted with reflux condenser, and 8 g of the bis(ethoxymethyl) ether of 1,3-propanediol was added. The mixture was heated in an oil bath for four hours. Fractionation: yield 35 ml of a substance of b.p. 78-112° and 6 g of a substance of b.p. 91° (11 mm) and n_D^{20} 1.4125; the residue was 3.2 g. The boiling point and refractive index of the second substance indicates that it is the bis(ethoxymethyl) ether of 1,3-propanediol. No alcoholysis products were detected in this case.

Alcoholysis of the Bis(butoxymethyl) Ether of Ethylene Glycol

A mixture of 100 ml of absolute butyl alcohol, 4.1 g of the bis(butoxymethyl) ether of ethylene glycol, and 2-3 drops of the bis(chloromethyl) ether of ethylene glycol was heated for four hours. Fractionation of the reaction products from an Arubzov flask gave 2.7 g of material of b.p. 59-62° (10 mm); n_D^{20} 1.4058; d_4^{20} 0.8384; and 0.8 g of material of b.p. 88-92° (10 mm); n_D^{20} 1.4220.

The substance of b.p. 59-62° (10 mm) corresponded to dibutoxymethane. The product of b.p. 88-92° (10 mm) was probably the monoether of ethylene glycol. We did not succeed in isolating any of the bis(butoxymethyl) ether.

Alcoholysis of the Bis(butoxymethyl) Ether of 1,2-Propanediol

A mixture of 4.7 g of the 1,2-propanediol ether and 100 ml of butyl alcohol was placed in a round-bottomed flask fitted with reflux condenser,. and two drops of the bis(chloromethyl) ether of 1,2-propanediol were added. The mixture was heated at the boiling point of the alcohol for three hours. Fractionation of the reaction products yielded butyl alcohol and also 2.1 g of dibutoxymethane, b.p. 60-63° (9 mm); n_D^{20} 1.4060.

Alcoholysis of the Bis(isobutoxymethyl) Ether of 1,3-Butanediol in Weakly Alkaline and Acid Media

Experiment 1. A mixture of a solution of sodium isobutoxide prepared by dissolving 0.1 g of sodium in 70 ml of isobutyl alcohol and 10.3 g of the bis(isobutoxymethyl) ether of 1,3-butanediol was heated at 106° for four hours. Fractionation yielded isobutyl alcohol and 9 g of the bis(isobutoxymethyl) ether of 1,3-butanediol, b.p. 132-134° (9.5 mm). In this case, therefore, no alcoholysis of the ether occurred.

Experiment 2. When a mixture of 70 ml of isobutyl alcohol, 8 g of the bis(isobutoxymethyl) ether of 1,3-butanediol, and two drops of the bis(chloromethyl) ether of 1,3-butanediol was heated, alcoholysis of the ether was observed. Fractionation of the alcoholysis products yielded isobutyl alcohol and diisobutoxymethane, b.p. 162-165° and n_D^{20} 1.4010. The literature gives b.p. 164.3°, n_D^{20} 1.4020 [12].

SUMMARY

1. A study has been made of the chloromethylation of 1,2- and 1,3-propanediols, and this has resulted in the preparation of the two corresponding bis(chloromethyl) ethers, which have not been described previously.

2. A study has been made of the reactions of the bis(chloromethyl) ethers of ethylene glycol, 1,2- and 1,3-propanediols, 1,3-butanediol and 2-butyne-1,4-diol with the methoxide, ethoxide, isopropoxide, butoxide, and isobutoxide of sodium. These reactions have resulted in the preparation of the corresponding bis(alkoxymethyl) ethers of the glycols, and also the mono(isopropoxymethyl) and mono(isobutoxymethyl) ethers of ethylene glycol, the mono(butoxymethyl) ether of 1,2-propanediol, and the compound $C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$.

3. It has been established that in the reactions of all of the investigated bis(chloromethyl) ethers of glycols with sodium butoxide and with sodium isobutoxide, by-products, i.e., dibutoxymethane and diisobutoxymethane, are formed. Also, in the reactions of the bis(chloromethyl) ether of ethylene glycol with sodium isobutoxide and of the bis(chloromethyl) ether of 1,2-propanediol with sodium butoxide, not only the corresponding acetals and bis(alkoxymethyl) ethers were formed, but also the corresponding mono(alkoxymethyl) ethers of these glycols. As a result of the reaction of the bis(chloromethyl) ether of ethylene glycol with sodium butoxide, in addition to dibutoxymethane and the bis(butoxymethyl) ether of the glycol, the following compound

was obtained:

$$C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9.$$

4. Hypotheses have been advanced in explanation of the formation of the acetals, monoethers of the glycols, and the substance

$$C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9.$$

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ISOMERIZATION OF TERPENE HYDROCARBONS BY THE ACTION OF SILICA GEL UNDER THE CONDITIONS OF ADSORPTIONAL ANALYSIS

B. A. Arbuzov and Z. G. Isaeva

In terpene chemistry the chromatographic method began to be adopted at the beginning of the thirties of this century, and the method is now fairly widely applied in the study of mono-, sesqui-, di-, and tri-terpenes [1-11]. The sorbent generally used for the chromatography of terpene compounds is aluminum oxide, although other sorbents have been used, e.g. activated charcoal and, very rarely, silica gel. The main, determining factor in the application of one or other sorbent is its chemical inertness toward the substances to be chromatographed, but the majority of substances that are used as sorbents are active catalysts for reactions of isomerization, polymerization, oxidation, splitting, etc. There are numerous examples in the literature of the catalytic action of sorbents on substances undergoing separation [12].

In 1951 we began an investigation of the behavior of some terpene hydrocarbons on silica gel under the conditions of adsorptional analysis, with the object of determining the possibility of applying silica gel to the chromatographic separation of mixtures of terpene compounds. In a study of the behavior of separate terpene hydrocarbons toward silica gel, we found that, under the conditions of adsorptional analysis, α-pinene, Δ^3-carene, and dipentene are isomerized by silica gel. Among the isomerization products of α-pinene we found camphene, dipentene, and terpinolene, and among the isomerization products of dipentene, terpinolene and p-cymene were identified. Δ^3-Carene isomerized into dipentene, and via dipentene into terpinolene. The action of silica gel on α-pinene, Δ^3-carene, and dipentene was thus found to be analogous to the action of activated clays on these substances, a thorough investigation of which has been made by Tishchenko, Rudakov, and others.

The isomerization of terpene hydrocarbons under the action of clays was first observed by Gurvich [13] in 1915, who observed the isomerization of α-pinene in presence of fuller's earth: among the reaction products, together with a large amount of polyterpenes, he found camphene and traces of monocyclic terpenes. Tishchenko and Marga [14] confirmed Gurvich's results. Similar results were obtained by Tsutomu Kuvata [15] by the action of acidic Japanese clays on pinene. Venable [16] found, in 1932, that α-terpinene was formed when dipentene was heated with fuller's earth.

In 1933, Tishchenko and Rudakov [17], in a study of the action of various active clays on α-pinene, found the optimum conditions for the preparation of camphene in high yield. This reaction was later studied by Rudakov [15] in greater detail, and among the reaction products camphene (50-55%), fenchene (5-6%), monocyclic terpenes (30-40%), and polymers (5-10%) were found. Dipentene, according to Rudakov's results [18], is isomerized under the action of activated clay into terpinolene, which is then converted into α-terpinene under the action of the same catalyst; also, p-cymene, p-menthene, and polymers are formed in the reaction. Among the products formed during the isomerization of Δ^3-carene under the same conditions, dipentene, terpinolene, sylvestrene in very small amount, and polymers were found [19].

When camphene is heated in presence of activated clay, the main reaction products are polyterpenes; p-cymene and borneol were identified among the products [20]. The isomerization of terpene hydrocarbons was performed by Rudakov and coworkers at high temperatures, 160-180°. Hence, the isomerization of α-pinene, Δ^3-carene, and dipentene on silica gel under the conditions of adsorptional analysis is analogous to that occurring on activated clays, but considerably milder temperature conditions are required (6-10°).

α-Pinene, when passed through a silica-gel column, gave a mixture of reaction products, which was separated into 18 fractions by fractionation through a 24-plate column. The results are summarized in Table 1 and are presented graphically in Fig. 1. The fractions of zone A, which formed 10% by weight of the reaction products, consisted essentially of camphene; we did not establish the nature of the impurities present. The fractions of zone B (44%) consisted of pure camphene. The fractions of zone D consisted of dipentene. Zone C was an intermediate

Table 1

Fraction No.	B.p. in °C (pressure in mm Hg)		Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	52.5-53	(21)	5.8	1.4618	0.8656	1.63
II	53-54	(21)	13	1.4635	0.8657	3.67
III	54-54.5	(21)	11.9	1.4665	0.8650	3.37
IV	53-53.5	(19)	9.5	1.4684	0.8640	2.68
V	50.5-52	(12)	29	Crystal	—	8.98
VI	57.5	(22)	16.8	"	—	4.75
VII	59	(23)	86	"	—	24.29
VIII	63.5	(27)	9.7	"	—	2.74
IX	63.5-66	(27)	4.5	"	—	1.27
X	64.76	(25)	13.3	1.4730	0.8492	3.75
XI	76-76.5	(25)	35.9	1.4740	0.8419	10.15
XII	68	(17.5)	16.5	1.4727	0.8466	4.66
XIII	58	(12)	19.9	1.4733	0.8445	5.62
XIV	44	(7.5)	23.5	1.4720	0.8426	6.64
XV	41.5-44	(6.5)	10.7	1.4840	0.8545	3.02
XVI	44-45.5	(6.5)	13.1	1.4830	0.8556	3.71
XVII	45.5-47.5	(6.5)	12.9	1.4890	0.8822	3.65
	Residue		22	—	—	6.22

fraction, terpinolene formed 9% of the reaction products (zone E), and the residue (6%) was not investigated. Dipentene and terpinolene were identified by preparing their tetrabromides. Terpinolene is an isomerization product of dipentene, as was shown by a special experiment.

These results on the behavior of α-pinene on silica gel are in conflict with the statement of Tishchenko and Rudakov [17] concerning the indifference of "samples of highly active silica gel" toward pinene, which they made in the course of a discussion of the mechanism of the isomerizing action of various clays on pinene.

The results obtained in the study of the action of silica gel on dipentene under the conditions of adsorptional analysis are given in Table 2 and presented graphically in Fig. 2. As will be seen from Table 2, the isomerization of dipentene with silica gel yields a complex mixture of reaction products.

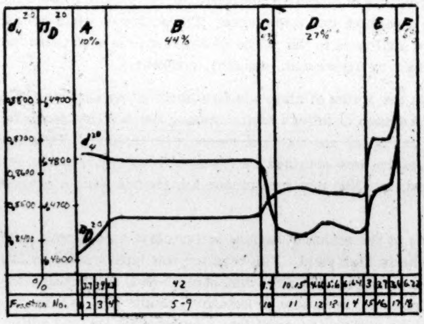

Fig. 1

Among the components of the fractions of zone A (16% by weight of the reaction products) were a small amount of p-cymene (identified by oxidation with chromic anhydride to terephthalic acid and the preparation from the latter of its dimethyl ester) and a product that polymerized when treated with sulfuric acid. The constants of Fraction II, which formed the bulk of zone A, were close to those of α-terpinene (b.p. 173.5-174.8° (755 mm); $d_4^{19.7}$ 0.8375; n_D^{19} 1.477). The substance of b.p. 57.5° (12 mm), however, gave no derivatives of α-terpinene: we did not succeed in preparing the maleic anhydride adduct of α-terpinene, nor the nitrosite of α-terpinene, and the nature of this substance (Fraction II) was not established. Zone B (34%) was unchanged dipentene: Fractions III and VII gave dipentene tetrabromide, m.p. 122-123° when brominated. Fractions of zone D contained terpinolene, identified by the preparation of its tetrabromide, m.p. 116-116.5°. The fractions of zone E and the residue remaining after the distillation were not investigated further.

These results show that under the conditions of adsorptional analysis, silica gel isomerizes dipentene into terpinolene, which undergoes further transformations, some idea of which can be formed from the fact that p-cymene was found among the reaction products.

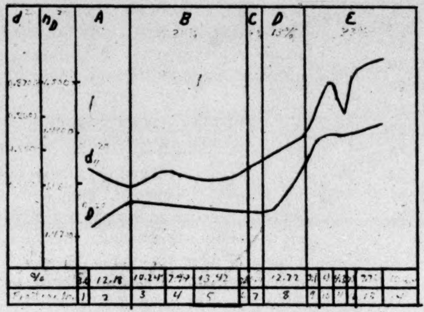

Fig. 2.

The results of the study of the action of silica gel on Δ^3-carene under the conditions of adsorptional analysis are presented in Table 3 and Fig. 3, from which it will be seen that only 37% isomerization occurs. The fractions of zones A anf B contained unchanged carene, and zone C contains intermediate fractions. The main component of the fractions of zone D (13% of the reaction products) was dipentene: bromination of these fractions yielded the tetrabromide, m.p. 122-123°. Fraction XII, represented in Fig. 3 by zone E (2%), contained terpinolene, which, as shown above, is formed by the isomerization of dipentene. The tetrabromide obtained from Fraction XII melted at 115-116°. The composition of the fractions making up zones F and G was not investigated.

TABLE 2

Fraction No.	B.p. in °C (pressure in mm Hg)	Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	54-57.5 (12.5)	4.6	1.4720	0.8451	3.57
II	57.5 (12)	15.7	1.4772	0.8395	12.18
III	56.5-57 (11.5)	13.2	1.4763	0.8449	10.24
IV	53.5 (10)	10.3	1.4760	0.8424	7.99
V	45 (7)	17.3	1.4753	0.8429	13.41
VI	40.5-42 (6)	3.6	1.4753	0.8461	2.79
VII	42-45 (6)	5.3	1.4750	0.8475	4.11
VIII	45-48 (6)	16.4	1.4838	0.8551	12.72
IX	59.5-61 (6)	5.1	1.4893	0.8652	3.96
X	65-66 (8)	5.2	1.4900	0.8713	4.03
XI	66 (8)	5.5	1.4897	0.8608	4.27
XII	63.5 (7.5)	2.7	1.4905	0.8732	2.10
XIII	63.5-65 (7)	10	1.4922	0.8768	7.76
	Residue	14	(viscous liquid)		

EXPERIMENTAL

The terpene hydrocarbons employed for the investigation of the behavior of such substances on silica gel under the conditions of adsorptional analysis, α-pinene, Δ^3-carene, and dipentene, were passed through a water-cooled silica-gel column. The height of the column was 1500 mm, and with respect to diameter the column was divided into three parts; the diameter was 12 mm in the lower part, 24 mm in the middle part, and 39 mm in the upper part. The silica gel was contained in the lower and middle parts of the column. The activity of the silica gel with respect to benzene was 9-11 ml. The weight ratios of terpene hydrocarbons and silica gel are given below for each separate case. For the elution of the hydrocarbons from the adsorbent, alcohol and water were used.

Isomerization of α-Pinene

Pinene [b.p. 40° (12 mm); n_D^{20} 1.4650; d_4^{20} 0.8596], separated from sulfate turpentine by fractionation through a 24-plate column, was passed through a silica-gel column. The activity of the silica gel with respect to benzene was 9.48 ml. The weight ratio of pinene to silica gel was 1 : 1.5. The catalyzate from four experiments (379 g) was fractionated twice through a 24-plate column, and the results are given in Table 1.

Bromination of the Fraction of b.p. 64-76° (25 mm)

A solution of 2 g of the substance of b.p. 64-76° (25 mm) in 7 ml of dry ether and 5 ml of amyl alcohol was added dropwise to a solution of 2 ml of bromine in 10 ml of dry ether, which was cooled with snow. The precipitate was crystallized from alcohol; m.p. 115-117°; after a second crystallization from alcohol, m.p. 122-122.5°;

Table 3

Fraction No.	B.p. in °C (pressure in mm Hg)	Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	41.5 (8)	12.8	1.4740	0.8586	6.12
II	46.5 (8.5)	11.9	1.4730	0.8596	5.69
III	46.5-47 (8.5)	6.3	1.4730	0.8604	3.01
IV	52-53 (11)	16.3	1.4727	0.8607	7.8
V	56.5 (13)	15.1	1.4726	0.8612	7.22
VI	58 (14)	5.4	1.4726	0.8612	2.58
VII	59 (14.5)	27.8	1.4720	0.8612	13.30
VIII	60.5 (16)	25.8	1.4720	0.8615	12.34
IX	65.5 (19)	23	1.4737	0.8564	11.00
X	66 (17.5)	22.3	1.4740	0.8440	10.67
XI	50 (8)	5.9	1.4740	0.8421	2.82
XII	46.5-48 (6.5)	5.5	1.4878	0.8579	2.63
XIII	47.5-48 (6)	5.1	1.5033	0.8653	2.44
	Residue	25.8			12.34

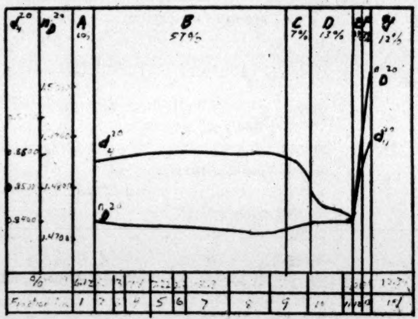

Fig. 3

after a third, m.p. 122-123°. A mixture test with dipentene tetrabromide showed no depression of melting point.

Bromination of the Fraction of b.p. 44° (7.5 mm)

The tetrabromide was prepared from 2 g of the substance of b.p. 44° (7.5 mm), 2 ml of bromine, 17 ml of ether, and 5 ml of amyl alcohol, and after three crystallizations from ethanol it melted at 121-122°. A mixture with dipentene dibromide melted at 121-122°.

Bromination of the Fraction of b.p. 41.5-44° (6.5 mm)

A solution of 2 g of the substance of b.p. 41.5-44° (6.5 mm) in 7 ml of ether and 5 ml of amyl alcohol was added to a cooled and constantly stirred solution of 3 ml of bromine in 10 ml of dry ether. Toward the end of the addition, a precipitate formed, the melting point of which after the first crystallization from alcohol was 106-111° (1.3 g). After the second crystallization from alcohol the melting point was 111-114° (0.9 g). After a third, it was 115-116° (0.5 g). The melting point of terpinolene tetrabromide is 116°.

Investigation of the Camphene Fraction, B.p. 52.5-53° (21 mm)

A mixture of 3.1 g of the substance of b.p. 52.5-53° (21 mm), 10 g of glacial acetic acid, and 0.3 g of sulfuric acid (sp.gr. 1.82) was heated in a water bath for 2 hours 30 minutes. The reaction mixture was cooled and poured into water; the upper layer was separated, washed with water, and hydrolyzed with a solution of 2 g of KOH in 15 ml of ethanol, the mixture being heated in a water bath for two hours. When the reaction mixture was poured into water, a resinous layer separated, and filtration yielded a small amount of substance, which was pressed off on filter paper and air-dried. It melted at 175-190° in a sealed capillary; it was readily soluble in the cold in alcohol, ether, and acetone. Melting point after recrystallization from gasoline, 194-197°. The weight of substance was 2.2 g (62.8% yield of isoborneol). The melting point of isoborneol from the Ural works was 193-199°, after recrystallization from gasoline of b.p. up to 130°. The peak on the specific gravity curve (Fig. 1, zone D) was caused by the high specific gravity of Fraction XII, as compared with Fractions XI and XIII, which consisted of dipentene. The residue remaining after distillation of the catalyzate was not investigated.

Isomerization of Dipentene.

Catalyzate (140 ml) obtained by passage of dipentene [b.p. 65° (15 mm); n_D^{20} 1.4730; d_4^{20} 0.8420] through a silica-gel column (activity of silica gel 11 ml) was fractionated through a 24-plate column into 14 fractions. The weight ratio of dipentene to silica gel was 1 : 1.4. The dimensions of the silica-gel column are given above. The results of the fractionation are given in Table 2.

Treatment of the Fraction of B.p. 57.5° (12 mm) with Sulfuric Acid.

The substance (3 ml) was shaken in a 10-ml cylinder with three portions of 70% sulfuric acid and then with a portion of 80% sulfuric acid, when the upper layer attained a constant volume of 1.9 ml. The upper layer (reddish brown) was separated, neutralized with a solution of sodium carbonate, washed with water, and extracted with ether. The ether extracts were dried with calcined potassium carbonate, the ether was driven off, and the residue was vacuum-distilled, yielding the fractions:

Fraction I, b.p. 55-57° (4.5 mm); 0.1 g; n_D^{20} 1.4824 (odor of cymene)
Fraction II, b.p. 140-150° (4 mm); 1 g; n_D^{20} 1.5155 (viscous liquid)

Oxidation of the Substance of B.p. 57.5° (12 mm) with Chromic Anhydride.

The substances taken for reaction were 2.1 g of the substance of b.p. 57.5° (12 mm), 10 g of chromic anhydride, 20 ml of 60% acetic acid, 10 ml of water, and 9 ml of sulfuric acid (sp.gr. 1.8). The substance was added carefully, with snow cooling, to a mixture of the remaining reaction components, and the resulting mixture was boiled gently for six hours. The mixture was cooled and poured into water, and the precipitate that formed was filtered off and dried; weight 0.03 g.

Preparation of Dimethyl Terephthalate.

A mixture of 0.03 g of terephthalic acid, obtained by the oxidation of the substance of b.p. 57.5° (12 mm), 5 ml of methanol, and 0.5 ml of sulfuric acid (sp.gr. 1.8) was boiled for five hours. The mixture was cooled and poured into water, and the flocs that were precipitated were filtered off, dried (weight 0.02 g), and crystallized from methanol; m.p. 137-139°. The substance of b.p. 57.5° (12 mm) gave no adduct with maleic anhydride. Bromination of Fractions III and VII yielded a tetrabromide of m.p. 122-123°.

Bromination of the Fraction of B.p. 45-48° (6 mm).

A solution of 5 g of the substance of b.p. 45-48° (6 mm) in 10 ml of ether and 8 ml of amyl alcohol was added to a cooled and constantly stirred solution of 5 ml of bromine in 25 ml of dry ether. After some time a precipitate formed; it was filtered off and crystallized from alcohol; weight 2.85 g, m.p. 115°. After a second crystallization, m.p. 116-116.5°.

Isomerization of Δ^3-Carene

Δ^3-Carene [b.p. 54° (12 mm); n_D^{20} 1.4730; d_4^{20} 0.8612] was passed twice through a silica-gel column (activity of silica gel 9.04 ml). The weight ratio of Δ^3-carene to silica gel was 1 : 2. Fractionation of 219 g of catalyzate through a 24-plate column yielded the fractions given in Table 3. The substance of b.p. 65.5° (19 mm) did not give dipentene tetrabromide when brominated.

Bromination of the Fraction of B.p. 66° (17.5 mm).

A solution of 2 g of the substance in 7 ml of ether and 5 ml of amyl alcohol was added to a cooled (snow and salt) and constantly stirred solution of 2 ml of bromine in 10 ml of ether. By the next day a crystalline precipitate had formed. It was filtered off and air-dried; weight 2.8 g. After two crystallizations from alcohol: m.p. 122-123°; weight 1.6 g. A mixture test with the tetrabromide obtained from dipentene showed no depression of melting point.

Bromination of the Fraction of B.p. 46.5-48° (6.5 mm).

The substances taken for reaction were 1.8 g of the substance of b.p. 46.5-48° (6.5 mm), 2.1 g of bromine, 19 ml of ether, and 4 ml of amyl alcohol. The procedure was similar to that described above. The melting point of the tetrabromide was 113-114° after the first crystallization and 115-116° after the second. The residue remaining after distillation of the catalyzate was not investigated.

SUMMARY

1. α-Pinene, Δ^3-carene, and dipentene are isomerized on silica gel under the conditions of adsorptional analysis: α-pinene is isomerized to camphene, dipentene, and terpinolene; Δ^3-carene to dipentene and terpinolene; and dipentene to terpinolene, which then undergoes further transformation. In the first two cases the terpinolene is formed by the isomerization of dipentene.

2. The isomerization of α-pinene, Δ^3-carene, and dipentene by silica gel under the conditions of adsorptional analysis is analogous to their isomerization by activated clays at temperatures close to the boiling points

of the hydrocarbons.

3. The results obtained for the isomerization of α-pinene by silica gel under the conditions of adsorptional analysis do not accord with the assertion by Tishchenko and Rudakov concerning the indifference of "samples of highly active silica gel" with respect to pinene.

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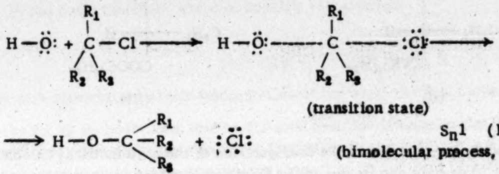
OPTICALLY ACTIVE ORGANOMERCURY COMPOUNDS

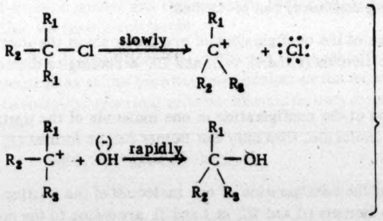
COMMUNICATION 2. MECHANISM OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

A. N. Nesmeyanov, O. A. Reutov, and S. S. Poddubnaya

The mechanism of nucleophilic substitution in the aliphatic series has been the subject of a large number of investigations. The results of numerous investigations, mainly on the kinetics of the hydrolysis of alkyl halides, led Ingold, Hughes, and coworkers [1] to the conclusion that there exist two different mechanisms for nucleophilic substitution at a saturated carbon atom:


(transition state)

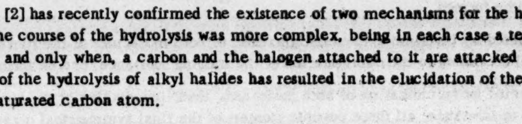
S_n1 (I)
(bimolecular process, or Walden inversion)


S_n1 (II)
(unimolecular process)

Swain [2] has recently confirmed the existence of two mechanisms for the hydrolysis of alkyl halides, but showed that the course of the hydrolysis was more complex, being in each case a termolecular process (reaction proceeds when, and only when, a carbon and the halogen attached to it are attacked simultaneously). Hence, an intensive study of the hydrolysis of alkyl halides has resulted in the elucidation of the mechanism of nucleophilic substitution at a saturated carbon atom.

At yet, however, there are no experimental facts known that would allow us to obtain an idea of the mechanism of electrophilic substitution at a saturated carbon atom, or, in particular, of its stereochemical course (inversion, racemization, maintenance of configuration?). The object of the present work was the investigation of the stereochemistry of electrophilic substitution at a saturated carbon atom.

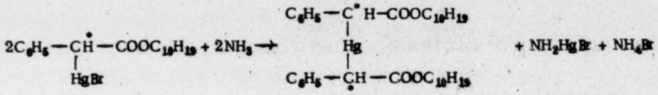
As an object for investigation we have chosen the electrophilic-substitution reaction occurring when mercuric bromide reacts with the di(−)-menthyl ester of mercuribis[phenylacetic acid]:



$$(C_6H_5-CH(COOC_{10}H_{19}))_2Hg + HgBr_2 \longrightarrow 2C_6H_5-CH(HgBr)-COOC_{10}H_{19}$$

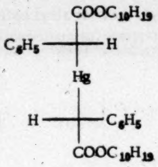
The symmetrical organomercury compounds that we required were obtained by the symmetrization of the pure diastereoisomeric (−)-menthyl esters of (bromomercuri)phenylacetic acid, the syntheses of which have been described in the preceding communication [3]. In the course of the preparation of the symmetrical starting compounds it was found to be necessary, and also possible, to solve the question of the mechanism of the symmetrization or organomercury compounds of the aliphatic series under the action of ammonia.

In the symmetrization of one of the diastereoisomers of the (−)-menthyl ester of (bromomercuri)phenylacetic acid

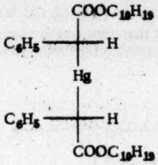


$$2C_6H_5-\overset{*}{C}H(HgBr)-COOC_{10}H_{19} + 2NH_3 \rightarrow (C_6H_5-\overset{*}{C}H-COOC_{10}H_{19})_2Hg + NH_2HgBr + NH_4Br$$

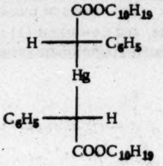
the formation of the following isomers of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] are formally possible:



(I)



(II)



(III)

1. If symmetrization is accompanied by preservation of the configuration of the asymmetrical carbon atoms in both molecules of the original substance, then only one isomer of the final symmetrical organomercury compound (I or III according to the configuration of the starting substance) can be formed.

2. If symmetrization is accompanied by preservation of the configuration of one molecule of the starting substance and racemization of the second molecule, then two isomers (I and II, or II and III, according to the configuration of the starting substance) can be formed.

3. If symmetrization is accompanied by preservation of the configuration of one molecule of the starting substance and inversion of the configuration of the second molecule, then only one isomer can be formed (II, irrespective of the configuration of the starting substance).

4. If symmetrization is accompanied by inversion of the configuration of one molecule of the starting substance and racemization of the second molecule, then two isomers (II and III, or I and II, according to the configuration of the starting substance) can be formed.

5. If symmetrization is accompanied by inversion of the configurations of both molecules of the starting substance, then only one isomer (III or I according to the configuration of the starting substance) can be formed.

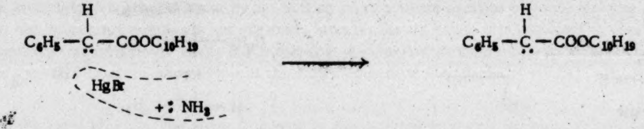
6. If symmetrization is accompanied by racemization of both molecules, then, irrespective of the configuration of the molecules of the starting substance, all three possible isomers of the final symmetrical organomercury compound must be formed.

Symmetrization of the (−)-menthyl ester of (bromomercuri)phenylacetic acid of $[\alpha]^{18}_{D}$ −95° and m.p. 161-162° (diastereoisomer I) results in the formation of one single isomer of the symmetrical organomercury compound, $[\alpha]^{18}_{D}$ −21.4° and m.p. 119-122°. Symmetrization of the (−)-menthyl ester of (bromomercuri)phenylacetic acid of $[\alpha]^{18}_{D}$ −49.3° and m.p. 152-154° (diasterioisomer II) results in the formation of a single but different isomer of the symmetrical organomercury compound, having $[\alpha]^{18}_{D}$ −7.7° and m.p. 118-120°.

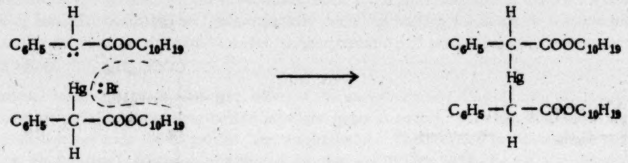
Variants 2, 4, and 6 are therefore eliminated, being in conflict with the fact of the formation of only one stereoisomer of the symmetrical organomercury compound. The fifth variant is impossible because the asymmetrical carbon atom of only one of the original molecules of organomercury salt is affected in the symmetrization. The third variant is eliminated by the fact that it would require the formation of the same isomer of the symmetrical organomercury compound in the symmetrization both of diastereoisomer I and of diastereoisomer II.

We must therefore conclude that symmetrization is accompanied by the preservation of the configurations of asymmetrical carbon atoms in both molecules of the original substance* (variant I). The symmetrization reaction may be represented as follows**:

a)



b)



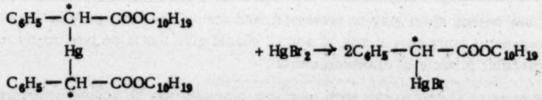
In this case, therefore, the electrophilic replacement

$$(R-HgBr + R-HgBr \xrightarrow{NH_3} R-Hg-R)$$

occurs with preservation of the configuration of the asymmetrical carbon atom.

As far as we have been able to discover from the literature, the mechanism of the symmetrization reaction has never been investigated: this is the first paper in this field. In all probability, the stereochemical course of the symmetrization of organomercury compounds of the aliphatic series under the action of alkali-metal alkoxides, alkali-metal cyanides and thiocyanates, hydrazine, and other nucleophilic reagents will be similar to that of the reactions we have investigated.

As we now had pure diasteriomeric di-(−)-menthyl esters of mercuribis[phenylacetic acid] (obtained by the symmetrization of the pure diastereoisomers of the (−)-menthyl ester of (bromomercuri)phenylacetic acid), we were able to study the reactions of these substances with mercuric bromide, which are electrophilic-substitution reactions:***



$$\begin{matrix} C_6H_5-\overset{*}{C}H-COOC_{10}H_{19} \\ | \\ Hg \\ | \\ C_6H_5-\underset{*}{C}H-COOC_{10}H_{19} \end{matrix} + HgBr_2 \rightarrow 2C_6H_5-\underset{\displaystyle HgBr}{\overset{*}{C}H}-COOC_{10}H_{19}$$

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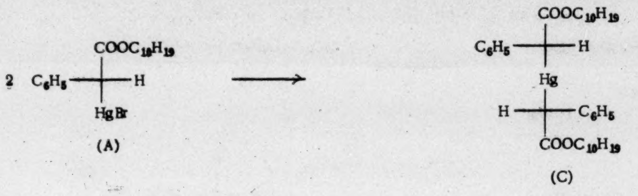
* The fact that the symmetrization reaction takes this course indicates that the free electron pair is able to fix the configuration of a carbon atom as in the case of sulfur [4].

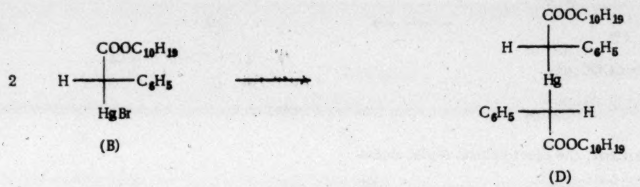
** That the rupture of the bond $\gt C\,:\,\vdots\, HgBr$ will proceed in the way indicated in the scheme will be seen from the following considerations: rupture of the bond as indicated by $\gt C\vdots\,:\,HgBr$ is impossible since it is associated with formation of the anion $\overset{(-)}{HgBr}$, and if the bond C — Hg were ruptured homolytically $\gt C\dot{:}\,HgBr$, then the free radical formed would take up a planar configuration, which would lead to the formation of two diastereoisomeric symmetrical organomercury compounds, instead of only one.

*** It can scarcely be doubted that reactions of this type, in which not only mercuric halide, but also highly dissociated mercury salts can take part [5], are electrophilic-substitution reactions.

The formation of the symmetrical organomercury compounds occurs, as has been shown above, with preservation of the configuration of the asymmetrical carbon atoms in both molecules of the original organomercury salt:



(I)



(II)

The reactions of the symmetrical organomercury compounds C and D with mercuric bromide may theoretically proceed in the following ways:

1. The configurations of both asymmetrical carbon atoms may be preserved. In that case the menthyl ester of (bromomercuri)phenylacetic acid obtained will be the diastereoisomer from which the given symmetrical organomercury compound was prepared (by symmetrization with ammonia). For example, in this case the symmetrical compound having $[\alpha]^{18}_{D}$ $-21.4°$, which was prepared by the symmetrization of $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$, for which $[\alpha]^{18}_{D}$ is $-96.5°$, will react with mercuric bromide to give $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$, for which $[\alpha]^{18}_{D}$ is again $-96.5°$; and the symmetrical compound having $[\alpha]^{18}_{D}$ $-7.7°$ (obtained from $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$ having $[\alpha]^{18}_{D}$ $-49.3°$) will react with mercuric bromide to give the organomercury salt having $[\alpha]^{18}_{D}$ $-49.3°$.

2. The configuration of one carbon atom may be preserved, and that of the other may be inverted. In that case both of the symmetrical organomercury compounds, C and D, should give the same product by reaction with mercuric bromide: an equimolecular mixture of diastereoisomers.

3. The reaction of the symmetrical compounds with mercuric bromide may be accompanied by preservation of the configuration of one carbon atom and racemization of the other half of the molecule*. In that case reaction of the symmetrical organomercury compound having $[\alpha]^{18}_{D}$ $-21.4°$, with mercuric bromide should give a mixture of diastereoisomers of $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$, consisting of 75% of the compound having $[\alpha]^{18}_{D}$ $-96.5°$ and 25% of the compound having $[\alpha]^{18}_{D}$ $-49.3°$; and reaction of the symmetrical compound having $[\alpha]^{18}_{D}$ $-7.7°$ with mercuric bromide should give a mixture of diastereoisomers of $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$ consisting of 75% of the compound having $[\alpha]^{18}_{D}$ $-49.3°$ and 25% of the compound having $[\alpha]^{18}_{D}$ $-96.5°$.

Actually, reaction of mercuric bromide both with the symmetrical compound having $[\alpha]^{18}_{D}$ $-21.4°$ and with the symmetrical compound having $[\alpha]^{18}_{D}$ $-7.7°$ yields an equimolecular mixture of diastereoisomers of $C_6H_5{-}\underset{HgBr}{CH}{-}COOC_{10}H_{19}$, which constitutes a proof that the reaction proceeds according to the second variant.

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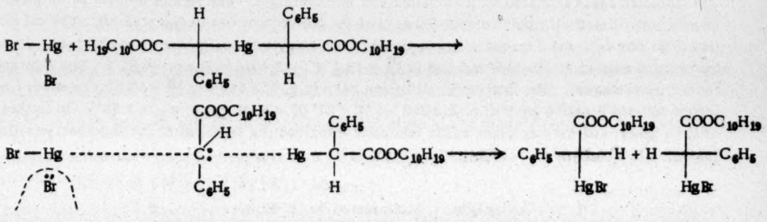
* As it is obvious that reaction with mercuric bromide is concerned with only one of two asymmetrical carbon atoms, we have not considered the following clearly improbable variants: 1) inversion of the configurations of both halves of the molecules; 2) inversion of the configuration of one half of the molecule and racemization of the other half; 3) racemization of both halves of the molecule.

Before this inference concerning the mechanism of the electrophilic substitution of the symmetrical organomercury compound may be regarded as reliable, it is necessary to remove one fundamental difficulty. Since the reaction investigated is brought about by the boiling of an acetone solution of equimolecular amounts of the symmetrical organomercury compound and mercuric bromide for six hours, it is necessary to consider the possibility of a secondary "racemization" of the unsymmetrical organomercury diastereoisomers formed. Such "racemization" might be expected to occur when either of the diastereoisomers of $C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOC_{10}H_{19}$ is boiled in acetone solution with mercuric bromide; the latter is present in the reaction mixture together with symmetrical and unsymmetrical organomercury compounds, for the reaction does not occur instantaneously, but over a fairly long period of time. In absence of mercuric bromide, no "racemization" occurs in boiling alcoholic or acetone solutions of the symmetrical and unsymmetrical diastereoisomers, as the possibility of separating the diastereoisomers by fractional crystallization shows.

A special investigation showed that, whereas the unsymmetrical diastereoisomer having $[\alpha]^{18}_{D}-95°$, for example, fully retained its rotation after being boiled for eight hours in acetone solution, a six-hour boil of the acetone solution with mercuric bromide led to partial "racemization" *. The rotatory power became $[\alpha]^{18}_{D}-80.2°$ (the rotatory power of the equimolecular mixture of diastereoisomers was $[\alpha]^{18}_{D}-73°$). Hence, the reaction of $HgBr_2$ with $C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOC_{10}H_{19}$ is slow. This gave us reason to hope that in a mixture of symmetrical organomercury compounds, unsymmetrical organomercury compound, and mercuric bromides, the latter would react with the symmetrical compound without effecting $C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOC_{10}H_{19}$.

A special experiment confirmed this supposition. In an eight-hour boil of an acetone solution of equimolecular amounts of mercuric bromide and the symmetrical organomercury compound together with twice the amount of the pure diastereoisomer of $C_6H_5-\underset{\substack{|\\ HgBr}}{CH}-COOC_{10}H_{19}$ having $[\alpha]^{18}_{D}-96°$, the mercuric bromide reacted only with the symmetrical compound, without affecting the unsymmetrical compound. On the basis of these experiments it may be definitely asserted that in the course of the reaction of di-(−)-menthyl esters of mercuribis[phenylacetic acid] with mercuric bromide there is no "racemization" of the unsymmetrical diastereoisomers.

The formation of an equimolecular mixture of unsymmetrical diastereoisomers A and B by the reaction of the symmetrical diastereoisomers C and D with mercuric bromide proves, therefore, that these electrophilic-substitution reactions at a saturated carbon atom are accompanied by inversion of the configuration at this carbon atom:



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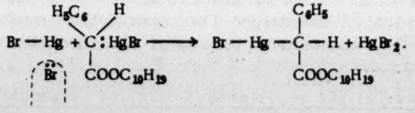
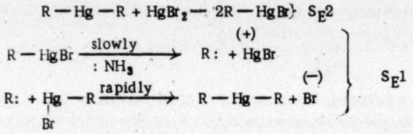
* On the basis of this fact we may already advance the hypothesis that the electrophilic substitution of an isomer of the unsymmetrical organomercury compound by mercuric bromide proceeds with inversion of configuration:



Hence, the electrophilic-substitution reaction of mercuric chloride with di-(−)-menthyl esters of mercuribis[phenylacetic acid] is accompanied by inversion of the configuration of the asymmetrical carbon atom, and the reaction of symmetrization of menthyl esters of (bromomercuri)phenylacetic acid are also electrophilic-substitution reactions, occurring with preservation of configuration. These circumstances can be understood if it is supposed that the mechanism of electrophilic substitution at a saturated carbon atom can vary according to the nature of the hydrocarbon radical at the atom (or group of atoms) being substituted and to the nature of the solvent, as is true of nucleophilic substitution. In that case, an electrophilic-substitution reaction proceeding with preservation of configuration must correspond to nucleophilic-substitution reactions proceeding by mechanism S_N1 (more accurately, by the "carbonium mechanism" [2]), and an electrophilic-substitution reaction proceeding with inversion of configuration must correspond to nucleophilic-substitution reactions proceeding by mechanism S_N2 (more accurately, by the "mechanism of direct substitution" [2]).

Whereas S_N1 nucleophilic-substitution reactions, e.g. the hydrolysis of alkyl halides, go readily in a medium of polar electrophilic substances, e.g. in formic acid, S_E1 electrophilic-substitution reactions of organomercury (and other organometallic) compounds should be facilitated by the presence of polar nucleophilic substances, such as ammonia, and this was found to be true in one of the cases that we investigated.

The difference in the stereochemical courses of the electrophilic-substitution reactions that we investigated is therefore to be explained, in our opinion, by difference in mechanism:



$$R-Hg-R + HgBr_2 \longrightarrow 2R-HgBr \Big\} \; S_E2$$

$$\left.\begin{array}{l} R-HgBr \xrightarrow[:\,NH_3]{\text{slowly}} \overset{(+)}{R:} + HgBr \\ R: + \underset{\displaystyle Br}{\underset{|}{Hg}}-R \xrightarrow{\text{rapidly}} R-Hg-R + \overset{(-)}{Br} \end{array}\right\} \; S_E1$$

This hypothesis, of course, requires verification with the aid of kinetic methods of investigation.

EXPERIMENTAL

1. Symmetrization of the isomer of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid having $[\alpha]_D^{18}$ − 95°

Dry ammonia was passed for two hours through a solution of 10 g of the (−)-menthyl ester of (bromomercuri)phenylacetic acid having m.p. 161-162° and $[\alpha]_D^{18}$ −95° in 150 ml of dry chloroform. The precipitate of chloroamidomercury was filtered off. The filtrate still contained some non-symmetrized organomercury compound, and was therefore again saturated with ammonia and left overnight. The further amount of chloroamidomercury that formed was filtered off (total amount 3.2 g), and the chloroform was evaporated off. The oil that remained solidified after one day, and 7 g (quantitative yield) of non-recrystallized product was obtained. After crystallization from methanol it melted at 112-115° and had $[\alpha]_D^{18}$ = 14.1° (C = 3.44; l = 2; α_D −0.87°). The substance was recrystallized further from ethanol. The first recrystallization gave m.p. 118-122°, $[\alpha]_D^{18}$ −17.5° (C = 4.05; l = 2; α_D −1.25°). The second recrystallization gave m.p. 119-122° $[\alpha]_D^{18}$ −21° (C = 4.06; l = 2; α_D = 1.33°). In further recrystallizations the rotatory power and melting point of the substance remained the same; after the third recrystallization they were m.p. 119-122°; $[\alpha]_D^{18}$ −21.4° (C = 3.32; l = 2; α_D −1.25°).

	Found %:	C 57.89; 57.65;	H 6.63; 6.51
$C_{36}H_{50}O_4Hg$.	Calculated %:	C 57.83;	H 6.77

The substance is described for the first time.

The filtrate from the first recrystallization did not contain any other isomer of the symmetrical organomercury compound: only the same isomer, somewhat contaminated and in small amount, m.p. 119-122° and $[\alpha]_D^{18}$ −21.4°, could be isolated from it. Hence as a result of the isomerization of the isomer of the (−)-menthyl ester of (bromomercuri)phenylacetic acid having $[\alpha]_D^{18}$ −95°, one single isomer is formed of the di-(−)-menthyl ester of mercuribis[phenylacetic acid], $[\alpha]_D^{18}$ −21.4° and m.p. 119-122°.

2. Symmetrization of the Isomer of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid having $[\alpha]_D^{18}$ − 49.3°

Under the conditions of the preceding experiment, 7 g of the (−)-menthyl ester of (bromomercuri)phenylacetic acid having m.p. 152-154° and $[\alpha]^{18}_{D}$ −49.3° yielded 4.5 g of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (93.8% yield). Recrystallization from methanol yielded 2.7 g of a substance of m.p. 118-120° and $[\alpha]^{18}_{D}$ −8.1 ± 0.15° (C = 3.38; l = 2; α_D −0.48°). Further recrystallizations did not affect the rotatory power and melting point; for example, after the second recrystallization they were m.p. 118-120°; $[\alpha]^{18}_{D}$ −7.7° ± 0.3° (C = 3.87; l = 2; α_D −0.52°).

Found %: C 57.98; 57.90; H 6.83; 6.70
$C_{36}H_{50}O_4Hg$. Calculated %: C 57.85; H 6.74

The substance is described for the first time.

3. Preservation of the Configuration of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid during Boiling in Acetone Solution

A solution of 0.7 g of the pure isomer of the (−)-menthyl ester of (bromomercuri)phenylacetic acid having m.p. 161.5-162.5° and $[\alpha]^{18}_{D}$ −95° in 50 ml of dry acetone was heated at the boil for eight hours. The acetone was evaporated off, and the remaining substance was crystallized from methanol, yielding a substance of m.p. 160-162° and $[\alpha]^{18}_{D}$ −94.4° (C = 0.754; l = 2; α_D −1.25°). The configuration of the molecules of the substance was therefore completely preserved under these conditions.

4. "Racemization of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid under the Action of Mercuric Bromide in Acetone

An acetone solution of 0.5 g (0.0009 mole) of the (−)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 158-159° and $[\alpha]^{18}_{D}$ −90.3°) and 0.35 g (0.001 mole) of mercuric bromide were heated at the boil for six hours. The acetone was evaporated off, and the residual substance was treated with chloroform, the undissolved mercuric bromide being filtered off. The substance that remained after evaporation of chloroform was recrystallized from methanol; m.p. 154-155°; $[\alpha]^{18}_{D}$ −80.2° (C = 0.74; l = 2; α_D −1.04°).

Under the action of mercuric bromide, therefore, slow "racemization" of the (−)-menthyl ester of (bromomercuri)phenylacetic acid occurs (the rotatory power of an equimolecular mixture of diastereoisomers is −73°).

5. Reaction of Mercuric Bromide with the Di-(−)-menthyl Ester of Mercuribis[phenylacetic acid] in Presence of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid

An acetone solution of a mixture of 0.75 g (0.001 mole) of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (m.p. 116-118°; $[\alpha]^{18}_{D}$ −5.5°), 1.1 g (0.002 mole) of the menthyl ester of (bromomercuri)phenylacetic acid (m.p. 161-162°; $[\alpha]^{18}_{D}$ −96°), and 0.36 g (0.001 mole) of mercuric bromide was heated at the boil for eight hours. The acetone was evaporated off, and the residual substance was crystallized from carbon tetrachloride, yielding a substance of m.p. 157-158° and $[\alpha]^{18}_{D}$ −85.9° ± 1° (C = 0.781; l = 2; α_D −1.18°).

Reaction of mercuric bromide with 0.75 g of the symmetrical compound yields 1.1 g of an equimolecular mixture of the (−)-menthyl esters of (+)- and (−)-(bromomercuri)phenylacetic acids having $[\alpha]^{18}_{D}$ −73°. If we suppose that the mercuric bromide did not "racemize" the 1.1 g of the menthyl ester of (bromomercuri)phenylacetic acid having $[\alpha]^{18}_{D}$ −96° that was added to the reaction mixture, the rotatory power of the product would be expected to be $\frac{-73°-96°}{2} = -84.5°$. As will be seen, this value is practically the same as the rotatory power of the substance formed in the reaction. Mercuric bromide, therefore, reacts with the symmetrical compound without affecting the unsymmetrical one, the configuration of which is preserved.

6. Reaction of Mercuric Bromide with the Diastereoisomers of the Di-(−)-menthyl Ester of Mercuribis[phenylacetic acid]

a) A mixture of 0.9 g (0.0012 mole) of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (m.p. 119-122°; $[\alpha]^{18}_{D}$ −21.4°) and 0.43 g (0.0012 mole) of mercuric bromide was heated in acetone solution at the boil for six hours. Completion of reaction was established by testing (with alkali) for the disappearance of mercuric chloride from the reaction mixture. The acetone was distilled off, and the residue was crystallized from carbon tetrachloride, yielding a substance of m.p. 155-157° and $[\alpha]^{18}_{D}$ −72.6° (C = 0.784; l = 2; α_D −1.00°). A mixture test with known (−)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 157-158°) gave no depression of melting point (mixture melted at 156-157°). Hence, as a result of the reaction an equimolecular mixture of diastereoisomerci menthyl esters of (bromomercuri)phenylacetic acid was formed.

b) A mixture of 0.95 g (0.0013 mole) of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (m. p. 118-120°; $[\alpha]^{18}_{D}$ −7.7°) and 0.46 g (0.0013 mole) of mercuric bromide was heated in acetone solution at the boil for six hours. Completion of reaction was determined as in the preceding experiment. The acetone was distilled off, and the residue was crystallized from carbon tetrachloride, yielding a substance of m.p. 157-158° and $[\alpha]^{18}_{D}$ −72.5° (C = 0.69; $\underline{l}$ = 2; α_D −0.87). A mixture test with known (−)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 157-158°) gave no depression of melting point (mixture melted at 157-158°). Hence, as a result of the reaction an equimolecular mixture of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid was formed.

SUMMARY

1. Two diastereoisomers of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] have been prepared in the pure state.

2. The mechanism of the symmetrization of organomercury compounds of the aliphatic series under the action of nucleophilic reagents has been elucidated.

3. The stereochemical course of an electrophilic-substitution reaction at a saturated carbon atom has been investigated for the first time, the examples studied being the symmetrization of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid and the reaction of the diastereoisomeric di-(−)-menthyl esters of mercuribis[phenylacetic acid] with mercuric bromide. It has been shown that the electrophilic-substitution reaction proceeds with retention of the configuration at the asymmetric carbon atom in the first case, and with inversion of the configuration in the second case.

4. A hypothesis has been advanced concerning the causes of the different stereochemical courses of the electrophilic-substitution reactions in the cases investigated.

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*See Consultants Bureau, Page 583.

GRIGNARD SYNTHESIS OF TETRAPHENYLSILANE, TETRA-p-TOLYSILANE, AND FLUOROTRI-p-TOLYLSILANE

V. S. Chugunov

It is known from the literature [1-3] that the synthesis of tetraarylsilanes that do not exhibit high steric-hindrance effects, such as tetraphenylsilane and tetra-p-tolylsilane, by the Grignard method may be effected only at elevated temperatures obtained by replacement of ether by a higher-boiling solvent. Under the usual conditions of synthesis, however, even when a large excess of arylmagnesium halide is boiled for a long time in an ether medium with tetrachlorosilane [4] or tetraethoxysilane [3], the reaction stops when the corresponding triarylhalo- or triarylethoxy-silane is formed. Our investigations have shown, however, that tetraphenyl- and tetra-p-tolyl-silanes can be obtained in good yields under the conditions of the Grignard synthesis when silicon tetrafluoride and excess of arylmagnesium halide are used as starting materials. When, for example, a mixture of silicon tetrafluoride and a two-fold excess of phenylmagnesium bromide was heated in a water bath, we obtained tetraphenylsilane in about 30% yield, about 14% of fluorotriphenylsilane [5] being obtained at the same time. Under the same conditions tetra-p-tolylsilane [6] was obtained in about 22% yield, and about 10% of fluorotri-p-tolylsilane, m.p. 103-104°, was obtained at the same time. If however, stoichiometric amounts of the reactants are used (1 mole of SiF_4 to 4 moles of p-tolylmagnesium bromide), then only fluorotri-p-tolylsilane is formed, even after prolonged boiling (as in the case of the synthesis of fluorotriphenylsilane).

EXPERIMENTAL

1. Tetraphenylsilane. Silicon tetrafluoride, obtained by dropping 300 ml of concentrated sulfuric acid into a mixture of 25 g of sodium fluosolicate and 15 g of finely-ground glass, was passed over a period of five hours into a constantly stirred solution of phenylmagnesium bromide prepared by dissolving 24 g of magnesium in a mixture of 500 ml of absolute ether and 157 g of bromobenzene. The ether was driven off, and the mixture was boiled in a water bath for four hours. The complex, cooled with ice water, was decomposed with 30% acetic acid, ether being added also. Ether-insoluble tetraphenylsilane separated, and was filtered off. Two crystallizations from toluene yielded 11.5 g (30% on the silicon tetrafluoride) of finely crystalline tetraphenylsilane, which we identified by its melting point (233-234°).

Fractionation of the ether extract yielded a fraction of b.p. 245-252°/30 mm, and from this, after crystallization from ether, we isolated 5.3 g of fluorotriphenylsilane in the form of large clear prisms, m.p. 63-64°, which is in accord with data in the literature [5].

2. Tetra-p-tolylsilane. Silicon tetrafluoride, obtained from 12.5 g of sodium fluosilicate, 150 ml of sulfuric acid, and 8 g of glass powder, was passed over a period of three hours into a solution of 0.5 mole of p-tolylmagnesium bromide prepared from 12 g of magnesium, 400 ml of ether, and 85 g of p-bromotoluene. Ether was removed, and the mixture was boiled in a water bath for five hours. The complex was cooled and decomposed as described above, and the tetra-p-tolylsilane that separated from ether solution was recrystallized from toluene, yielding 5 g (22%) of finely crystalline tetra-p-tolylsilane, m.p. 226-227°.

When the ether extract was fractionated, two fractions were collected. Fraction I, b.p. 205-214°/35 mm, was crystallized from ether, and 0.6 g of the by-product p,p'-bitolyl, m.p. 121°, was isolated. Fraction II (5.4 g; b.p. 245-252°/35mm) yielded 2.1 g (10% on the SiF_4 taken) of fluorotri-p-tolylsilane, m.p. 103-104°. Fluorotri-p-tolylsilane, like fluorotriphenylsilane, crystallizes from ether in the form of large clear prisms. Under atmospheric conditions it boils at 324-327° without decomposition. It is of good solubility in benzene, toluene, chloroform, and carbon tetrachloride.

Found %: Si 8.5; 8.1
$C_{21}H_{21}SiF$. Calculated %: Si 8.7
Found %: F 6.0; 6.2; M 328; 334
$C_{21}H_{21}SiF$. Calculated %: F 5.9; M 324

3. Fluorotri-p-tolylsilane. Silicon tetrafluoride, obtained from 25 g of sodium fluosilicate, 300 ml of concentrated sulfuric acid, and 15 g of glass powder, was passed over a period of five hours into an ethereal solution of p-tolylmagnesium bromide prepared from 12 g of magnesium and 85 g of p-bromotoluene. The ether was removed, and the mixture was boiled in a water bath for five hours. The complex was cooled and decomposed with 30% acetic acid. Under these conditions the separation of ether-insoluble tetra-p-tolylsilane was not observed. Fractionation of the ether extract yielded 24.6 g of a fraction of b.p. 246-252°/35 mm, and recrystallization of this from ether yielded 17.5 g (42% on the SiF_4 taken) of fluorotri-p-tolylsilane, the properties of which are given above.

SUMMARY

1. It has been established that, when silicon tetrafluoride reacts with a two-fold excess of phenyl- or p-tolyl-magnesium bromide under the conditions of the Grignard synthesis, the corresponding tetraarylsilane is obtained in good yield.

2. Fluorotri-p-tolylsilane has been synthesized for the first time, and some of its properties have been determined.

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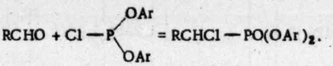
REACTIONS OF ALDEHYDES WITH PHOSPHONOUS AND PHOSPHINOUS CHLORIDES

M. I. Kabachnik and E. S. Shepeleva

In previous papers we have shown [1] that, when an aldehyde is heated with phosphorus trichloride in a sealed tube or autoclave at 160-250°, an α-chloro phosphonic dichloride is obtained:

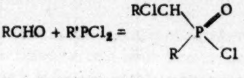
$$RCHO + PCl_3 = RCHCl - POCl_2.$$

If instead of phosphorus trichloride a diaryl phosphorochloridite is used, it is possible to obtain a diaryl 1-chloroalkylphosphonate in satisfactory yield [2]:



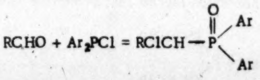
$$RCHO + Cl-P\begin{matrix}OAr\\ \\OAr\end{matrix} = RCHCl - PO(OAr)_2.$$

It was of interest to determine the extent to which our reaction was applicable to phosphonous and phosphinous chlorides, i.e., to substances already having a C—P bond in the molecule. If phosphonous dichlorides react like phosphorus trichloride, then α-chloro phosphinic chlorides should be formed. For example, from alkylphosphonous dichlorides and aldehydes, alkyl-1-chloroalkylphosphinic chlorides should be obtained:



$$RCHO + R'PCl_2 = \begin{matrix}RClCH & & O\\ & P & \\ R' & & Cl\end{matrix}$$

In a similar way, from diarylphosphinous chlorides, diaryl-1-chloroalkylphosphine oxides should be obtained:



$$RCHO + Ar_2PCl = RClCH - \overset{O}{\overset{\|}{P}}\begin{matrix}Ar\\ \\Ar\end{matrix}$$

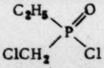
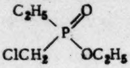
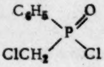
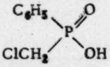
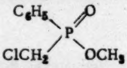
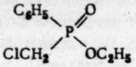
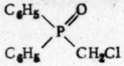
These conclusions were found to be correct. We investigated the reactions of paraformaldehyde with the most accessible phosphonous dichlorides, ethyl- [3] and phenyl-phosphonous dichlorides [4]. Ethylphosphonous dichloride and paraformaldehyde reacted when heated in a sealed tube at 200° for 2 hours 30 minutes, and gave a 36% yield of (chloromethyl)ethylphosphinic chloride (I). This substance has all of the properties of an acid chloride; thus, when it is poured into ethanol, the chlorine atom is smoothly replaced by an ethoxyl group, and ethyl (chloromethyl)ethylphosphinate (II) is formed.

The reaction of phenylphosphonous dichloride with paraformaldehyde requires more severe conditions: the tubes containing the mixture of reactants must be heated to 230-250°. (Chloromethyl)phenylphosphinic chloride (III) was obtained in 47% yield. When it was poured into cooled absolute methanol or ethanol, the corresponding esters (V and VI) were obtained; they are colorless glycerollike liquids, readily soluble in water and organic solvents. Hydrolysis of (chloromethyl)phenylphosphinic chloride was accompanied by some evolution of heat, and crystalline (chloromethyl)phenylphosphinic acid (IV) was obtained.

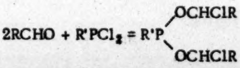
Diphenylphosphinous chloride reacted with paraformaldehyde when heated in a sealed tube at 240-250° for two hours, and a high-boiling substance, (chloromethyl)diphenylphosphine oxide, was obtained in 40% yield. The constants of the substances obtained are given in the table.

We consider that the mechanism of the formation of phosphinic chlorides from paraformaldehyde and phosphonous dichlorides is quite similar to the mechanism of the reaction of phosphorous trichloride with aldehydes, which we have examined previously [1]. That is to say, in the first stage, which occurs already in the cold, two

TABLE

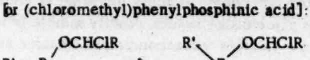
No.	Formula	B.p. in °C (pressure in mm Hg)	M.p. (°C)	d_4^{20}	n_D^{20}	MR_D	
						Found	Calculated*
(I)		83-84 (3.5)	–	1.3628	1.4937	34.35	34.32
(II)		78-78.5 (3)	–	1.1632	1.4570	39.92	39.96
(III)		116-117 (2)	47-49	–	–	–	–
(IV)		–	93-93.5	–	–	–	–
(V)		125-126 (2.5)	–	1.2654	1.5409	50.76	50.21
(VI)		132-134 (2.5)	–	1.2329	1.5275	54.53	54.83
(VII)		146-147 (2)	122-124	–	–	–	–

molecules of the aldehyde add to the phosphonous dichloride with formation of a bis(chloroalkyl) ester of a phosphonous acid:



$$2RCHO + R'PCl_2 = R'P(OCHClR)_2$$

This substance should be extremely prone to undergo the Arbuzov rearrangement, which will occur under the influence of the alkyl-halide function contained in the ester grouping, no addition of alkyl halide being necessary: on the one hand, Arbuzov and Rizpolozhensky [5] have recently shown that ethylphosphonous esters readily undergo the Arbuzov rearrangement, and the readiness with which phenylphosphonous esters undergo the rearrangement has long been known from the work of A. E. Arbuzov [6]; and on the other hand, Abramov [7] has shown that α-chloro esters bring about the Arbuzov rearrangement of trialkyl phosphites already in the cold. There can be no doubt, therefore, that the bis(chloromethyl) (or similar) ester of ethyl- or phenyl-phosphonous acid, once formed, will quickly undergo Arbuzov rearrangement with formation of the chloromethyl (chloroalkyl) ester of a (chloromethyl)-ethylphosphinic acid [or (chloromethyl)phenylphosphinic acid]:



How the rearrangement will occur, intra- or inter-molecularly, cannot be predicted. In the first case the intermediate phosphonium compound must be cyclic:

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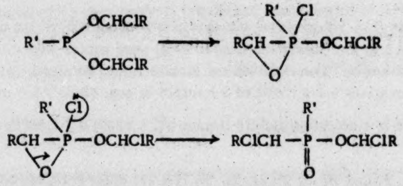
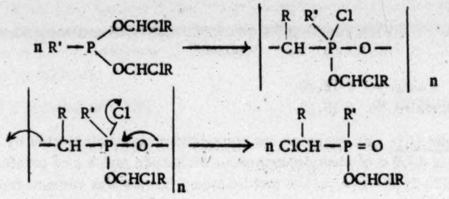
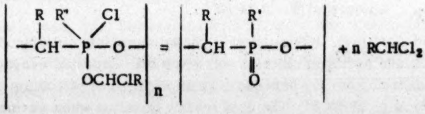
*The atomic refraction of phosphorus in phosphinic acid derivatives is not known. We have deduced the value $AR_P = 4.85$ from a limited number of data, and it must therefore be regarded as a preliminary value.


[A]

In the second case the intermediate phosphonium compound must have a polymeric character, since it is formed by the alkylation at the phosphorus atom of one molecule by the chloroalkyl group of another. If we represent only the repeating unit of the polymeric phosphonium compound, the intermolecular rearrangement can be represented as:

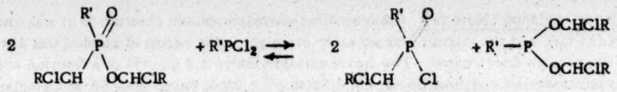


The formation (as in the case of the reaction of paraformaldehyde with phosphorus trichloride [1]) of a large amount of undistillable residue indicates that some intermolecular reaction undoubtedly occurs, for only then could a polymeric residue be formed; it is formed in the second stage of the Arbuzov rearrangement by the elimination of the chloroalkyl side groups without effect on the main chain:



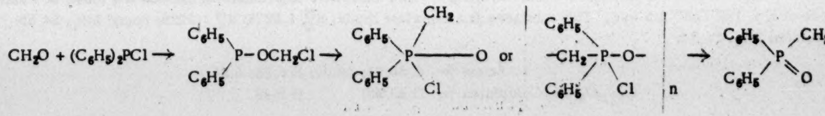
Whether there is simultaneous intramolecular alkylation in accordance with scheme A it is as yet impossible to say.

The last stage in the formation of an alkyl(chloroalkyl)phosphinic chloride is the metathetic reaction of the Arbuzov-rearrangement product with a second molecule of the phosphonous dichloride:



The final reaction product, an alkyl-1-chloroalkylphosphinic chloride, and some fresh bis(chloroalkyl) ester of a phosphonous acid, $R'-P(OCHClR)_2$, are formed. The latter again undergoes the Arbuzov rearrangement, etc., until the whole of the phosphonous dichloride has reacted.

We give our proposed scheme for the mechanism of the reaction of diphenylphosphinous chloride with paraformaldehyde without comment:



EXPERIMENTAL

(Chloromethyl)ethylphosphinic Chloride (I). We prepared our ethylphosphonous dichloride by Michaelis's method [3]. Ethylphosphonous dichloride (13.1 g) and paraformaldehyde (3 g) were mixed with cooling, sealed in a tube, and heated at 200° for 2 hours 30 minutes. The light-yellow mobile liquid obtained was vacuum-fractionated, and after four successive fractionations 5.8 g (36%) of a fraction of b.p. 83-84°/3.5 mm was obtained.

(Chloromethyl)ethylphosphinic chloride is a colorless mobile liquid; n^{20}_D 1.4937; d^{20}_4 1.3628; Found MR_D 34.35; Calculated MR_D 34.32.

Found %: C 22.61; 22.70; H 4.28; 4.38; P 18.76; 19.17
$C_3H_7OPCl_2$. Calculated %: C 22.35; H 4.34; P 19.25

Ethyl (chloromethyl)ethylphosphinate (II). (Chloromethyl)ethylphosphinic chloride (2.6 g) was poured into cooled absolute ethanol (12 ml), and the mixture was set aside overnight. The excess of alcohol was distilled off, and the residue was vacuum-fractionated. Two fractionations yielded 1.5 g (72%) of a substance of b.p. 78-78.5°/3 mm.

Ethyl (chloromethyl)ethylphosphinate is a colorless liquid; d^{20}_4 1.1632; n^{20}_D 1.4570; Found MR_D 39.92; Calculated MR_D 39.96.

Found %: P 18.34
$C_5H_{12}O_2PCl$. Calculated %: P 18.19

(Chloromethyl)phenylphosphinic Chloride (III). We prepared our phenylphosphonous dichloride by Michaelis's method, as improved by Dye [4]. A mixture of 17.9 g of phenylphosphonous dichloride and 3 g of paraformaldehyde was heated in a sealed tube for two hours at 230-240°. The yellow mobile liquid formed was vacuum-fractionated, and yielded 9.9 g (47%) of a substance of b.p. 116-117°/2 mm, which rapidly solidified in the receiver.

(Chloromethyl)phenylphosphinic chloride forms white hygroscopic crystals, melting in a sealed capillary at 47-49°.

Found %: P 14.46; 14.51
$C_7H_7OPCl_2$. Calculated %: P 14.83

(Chloromethyl)phenylphosphinic Acid (IV). (Chloromethyl)phenylphosphinic chloride (2 g) was dissolved in water (15 ml); some heat was evolved, and hydrogen chloride was given off. Repeated evaporation with water yielded some crystals, and these were recrystallized from dry benzene with an addition of petroleum ether, and then again recrystallized from water. Yield 60%; m.p. 93-93.5°. The acid readily dissolves when warmed with absolute alcohol; it is difficultly soluble in benzene, petroleum ether, water, and ether.

Found %: C 44.13; 44.44; H 4.43; 4.44; P 16.10; 15.90
$C_7H_8O_2PCl$. Calculated %: C 44.09 H 4.20 P 16.28

Methyl (chloromethyl)phenylphosphinate (V). (Chloromethyl)phenylphosphinic chloride (3 g) was dissolved in cooled absolute ethanol (15 ml), and the mixture was set aside overnight. The excess of alcohol was distilled off, and the reaction mixture was vacuum-fractionated. Two fractionations yielded 1.4 g (47%) of a fraction boiling at 125-126° at 2.5 mm. This substance is a colorless liquid; n^{20}_D 1.5409; d^{20}_4 1.2654; Found MR_D 50.76. Calculated MR_D 50.21.

Found %: P 14.95; 14.82
$C_8H_{10}O_2PCl$. Calculated %: P 15.17

Ethyl (chloromethyl)phenylphosphinate (VI). (Chloromethyl)phenylphosphinic chloride (5 g) was dissolved in cooled absolute ethanol (20 ml) and set aside overnight. Two successive fractionations yielded 2 g (48%) of a substance of b.p. 132-123°/2.5 mm. This substance is a colorless liquid; n^{20}_D 1.5275; d^{20}_4 1.2329; Found MR_D 54.53; Calculated MR_D 54.83.

Found %: C 50.01; 50.00; H 5.66; 5.65
$C_9H_{12}O_2PCl$. Calculated %: C 49.43; H 5.49

(Chloromethyl)diphenylphosphine Oxide (VII). We prepared our diphenylphosphinous chloride by the method of Meisenheimer and coworkers [8]. A mixture of 2.2 g of diphenylphosphinous chloride and 0.3 g of paraformaldehyde was heated in a sealed tube for two hours at 230-240°. Two fractionations yielded 0.8 g (40%) of a substance of b.p. 146-147°/2 mm, which crystallized when cooled to below its melting point. The substance forms white hygroscopic crystals, which melt at 122-124° to a turbid liquid that clears at 135-137°.

Found %: P 12.30; 11.97

$C_{13}H_{12}OPCl$. Calculated %: P 12.37

SUMMARY

1. It has been shown that paraformaldehyde reacts with alkyl- and aryl-phosphonous dichlorides with formation of alkyl- and aryl-(chloromethyl)phosphinic chlorides; the free phosphinic acids and their esters have been prepared.

2. It has been shown that diphenylphosphinous chloride reacts with paraformaldehyde with formation of (chloromethyl)diphenylphosphine oxide.

3. It has been suggested that the mechanism of the reaction of phosphonous and phosphinous chlorides with aldehydes is similar to that of the reaction of phosphorus trichloride with aldehydes and includes the stages of the formation of a bis(1-chloroalkyl)phosphonous ester, its Arbuzov rearrangement, and the replacement of ester groupings by chlorine.

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Institute of Organic Chemistry of the USSR Academy
of Sciences

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[3] A. Michaelis, Ber. 13, 2174 (1880).

[4] A. Michaelis, Ann. 181, 265 (1876); W. T. Dye, J. Am. Chem. Soc. 70, 7, 2595 (1948).

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[6] A. E. Arbuzov, J. Gen. Chem., 4, 898 (1934).

[7] V. S. Abramov, E. V. Sergeeva, and I. V. Chelpanova, J. Gen. Chem., 14, 1030 (1944).

[8] Y. Meisenheimer, H. Glawe, H. Greeske, A. Shorning, E. Vieweg, Ann. 449, 228 (1926).

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* See Consultants Bureau, Page 747.

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NEW METHOD FOR THE SYNTHESIS OF 1-AMINOALKYLPHOSPHONIC ACIDS

COMMUNICATION 1

M. I. Kabachnik and T. Ya. Medved

Until recently 1-aminoalkylphosphonic acids were difficultly accessible substances. The authors of this paper prepared the first member of this class of compounds, aminomethylphosphonic acid, from diethyl chloromethylphosphonate by heating it with 25% aqueous ammonia in a sealed tube at 150° for two hours [1]:

$$ClCH_2PO(OC_2H_5)_2 + 3NH_3 + H_2O = NH_2CH_2PO(OC_2H_5)ONH_4 + NH_4Cl + C_2H_5OH$$

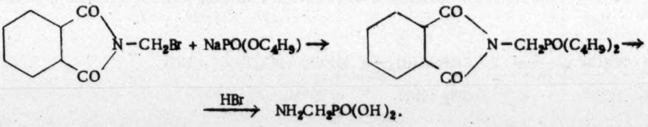
and then hydrolyzing the partial ester formed. The required ester of chloromethylphosphonic acid is readily synthesized in two stages from paraformaldehyde and phosphorus trichloride (first stage), and then alcohol (second stage), a method that was developed in our laboratory by Kabachnik and Shepeleva [2]:

$$PCl_3 + CH_2O = ClCH_2POCl_2;$$

$$ClCH_2POCl_2 + 2C_2H_5OH = ClCH_2PO(OC_2H_5)_2 + 2HCl.$$

The whole synthesis of aminomethylphosphonic acid was therefore effected in three stages.

A few other cases of the synthesis of aminoalkylphosphonic acids have been described. Aminomethylphosphonic acid, for example, has been prepared from N-bromomethylphthalimide and sodium dibutyl phosphite, with subsequent hydrolysis of the phthalimide derivative with hydrobromic acid [3]:

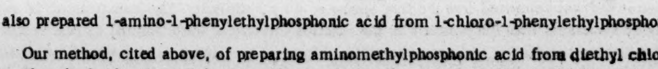


Also, according to patent literature, aminomethylphosphonic acid may be prepared from hydroxymethyl derivatives of amides and phosphorus trichloride; the acid chloride of the acylated amino acid that is first formed is subjected to complete hydrolysis [4]:

$$RCONHCH_2OH + PCl_3 \rightarrow RCONHCH_2OPCl_2 \rightarrow RCONHCH_2POCl_2 \xrightarrow{\text{hydrolysis}} NH_2CH_2PO(OH)_2.$$

Kosolapoff [5] synthesized *α*-aminobenzylphosphonic acid by the use of the p-nitrophenylhydrazone of diethyl benzoylphosphonate, which he prepared by Kabachnik and Rossyskaya's method [6]; for this, deep-seated reduction of the p-nitrophenylhydrazone was necessary:

$$C_6H_5COCl + P(OC_2H_5)_3 \rightarrow C_6H_5COPO(OC_2H_5)_2 \rightarrow$$



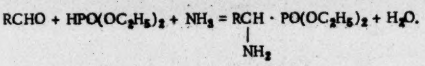
$$\xrightarrow{ArNHNH_2} \underset{\underset{N\cdot NHAr}{\|}}{C_6H_5C}-PO(OC_2H_5)_2 \rightarrow \underset{\underset{NH_2}{|}}{C_6H_5CH}-PO(OC_2H_5)_2 \xrightarrow{H_2O} \underset{\underset{NH_2}{|}}{C_6H_5CH}PO(OH)_2$$

He also prepared 1-amino-1-phenylethylphosphonic acid from 1-chloro-1-phenylethylphosphonic acid [7].

Our method, cited above, of preparing aminomethylphosphonic acid from diethyl chloromethylphosphonate, although undoubtedly simpler than the other methods indicated, demands much labor and time, particularly in the separation of the reaction products from the reaction mixture. None of the described syntheses of amino phosphonic acids is generally applicable, and all of them are multistage processes, so that amino phosphonic acids remain difficultly accessible.

It is, however, desirable to develop a direct and simple synthesis of compounds of this class. It is sufficient to point out that *a*-amino phosphonic acids are phosphorus analogs of *a*-amino carboxylic acids, the biological significance of which is enormous. The study of the properties of *a*-amino phosphonic acids is however greatly hindered by the absence of a good general method of synthesis.

Last year we reported that we had found a new method for the synthesis of esters of *a*-amino phosphonic acids in one stage by a reaction between an aldehyde, a dialkyl hydrogen phosphite, and ammonia [8]:

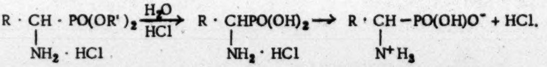


$$RCHO + HPO(OC_2H_5)_2 + NH_3 = \underset{NH_2}{\underset{|}{RCH}} \cdot PO(OC_2H_5)_2 + H_2O.$$

In the examples investigated we used benzaldehyde and piperonal, and diethyl and dibutyl hydrogen phosphites.

Later, a communication from Fields [9] appeared concerning the preparation of esters of *a*-amino phosphonic acids by the action of amines (primary and secondary) and aldehydes on dialkyl hydrogen phosphites. The author states that the reaction is applicable only to the synthesis of esters of aminoalkylphosphonic acids that are substituted at the nitrogen (Fields did not prepare the free amino phosphonic acids). We, however, have found that the synthesis of unsubstituted amino phosphonic acids—the most interesting compounds of this class, as will be shown in this paper—can be effected with equal success.

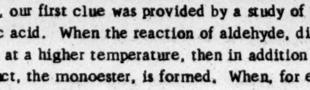
The present paper is devoted to a more detailed investigation of the reaction of aromatic aldehydes with ammonia and dialkyl hydrogen phosphites. It was first of all shown to what extent the reaction is a general one. We synthesized amino phosphonic acids from benzaldehyde, p-tolualdehyde, p-isopropylbenzaldehyde, p-anisaldehyde, piperonal, and vanillin. The reaction was carried out by heating equimolecular amounts of aldehyde and dialkyl hydrogen phosphite with a small excess of a 10% alcoholic solution of ammonia in sealed tubes in a water bath, and the corresponding esters of *a*-amino phosphonic acids were formed in accordance with the above equation. In order to isolate them from the reaction mixture, we converted these esters into well crystallizing salts—the hydrochloride or picrate. In Table 1 we give the salts of esters of *a*-amino phosphonic acids obtained in this way. From these salts of the esters the free acids were obtained by heating them with diluted (1 : 1) hydrochloric acid at 110-130° for several hours. The ester groups were then hydrolyzed, and when the solution was evaporated to dryness, the hydrochloride of the amino acid was converted into the internal salt with evolution of hydrogen chloride:



$$R \cdot \underset{NH_2 \cdot HCl}{\underset{|}{CH}} \cdot PO(OR')_2 \xrightarrow[HCl]{H_2O} R \cdot \underset{NH_2 \cdot HCl}{\underset{|}{CH}}PO(OH)_2 \longrightarrow R \cdot \underset{N^+H_3}{\underset{|}{CH}} - PO(OH)O^- + HCl.$$

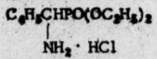
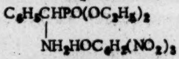
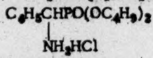
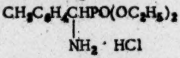
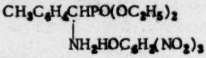
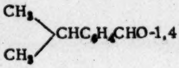
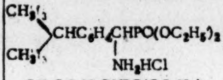
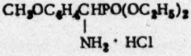
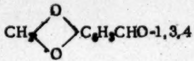
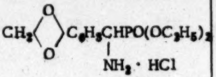
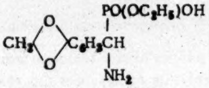
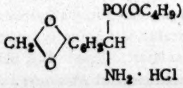
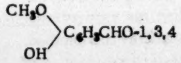
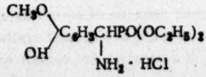
The free amino phosphonic acids obtained in this way are presented in Table 2. They are all high-melting crystalline solids, having powerful acid properties and titrating as monobasic acids.

With regard to the mechanism of the formation of amino phosphonic acids from aldehydes, dialkyl hydrogen phosphites, and ammonia, our first clue was provided by a study of the effect of the reaction temperature on the yield of amino phosphonic acid. When the reaction of aldehyde, dialkyl hydrogen phosphite, and ammonia is carried out not at 100°, but at a higher temperature, then in addition to the diester of the amino acid, some of the partially hydrolyzed product, the monoester, is formed. When, for example, piperonal was heated at 130-140° with alcoholic ammonia and diethyl hydrogen phosphite, not only the diethyl ester of the corresponding amino acid was formed, but also an acid ester of structure



This substance was neutral and was converted into the free amino acid by hydrolysis. The formation of the monoester must undoubtedly be associated with the presence in the reaction mixture of water formed by reaction of ammonia with the aldehyde and the dialkyl hydrogen phosphite. When the reaction is carried out at room temperature, an insignificant amount of aminoalkylphosphonic ester is formed, the main product being a hydroxyalkylphosphonic ester (the case examined was benzaldehyde and diethyl hydrogen phosphite). Hence, in presence of

TABLE 1

Aldehyde	Dialkyl hydrogen phosphite	Salt isolated	M.p. (°C)	Yield %
C_6H_5CHO	$HPO(OC_2H_5)_2$	 $C_6H_5\underset{NH_2\cdot HCl}{CH}PO(OC_2H_5)_2$	158-159	38
		 $C_6H_5\underset{NH_2HOC_6H_2(NO_2)_3}{CH}PO(OC_2H_5)_2$	174	–
	$HPO(OC_4H_9)_2$	 $C_6H_5\underset{NH_2HCl}{CH}PO(OC_4H_9)_2$	149	20
$CH_3C_6H_4CHO$-1,4	$HPO(OC_2H_5)$	 $CH_3C_6H_4\underset{NH_2\cdot HCl}{CH}PO(OC_2H_5)_2$	149	8
		 $CH_3C_6H_4\underset{NH_2HOC_6H_2(NO_2)_3}{CH}PO(OC_2H_5)_2$	187	16
	$HPO(OC_2H_5)_2$		167	35
$CH_3OC_6H_4CHO$-1,4	$HPO(OC_2H_5)_2$	 $CH_3OC_6H_4\underset{NH_2\cdot HCl}{CH}PO(OC_2H_5)_2$	160	32
	$HPO(OC_2H_5)_2$		145	43
			240	–
	$HPO(OC_4H_9)_2$		160	14
	$HPO(OC_2H_5)_2$		181	32

ammonia, dialkyl hydrogen phosphites react with aldehydes forming in the cold hydroxyalkylphosphonic ester, and at higher temperatures—aminoalkylphosphonic esters.

The formation of hydroxylakylphosphonic esters from dialkyl hydrogen phosphites and aldehydes under the catalytic action of sodium alkoxide has been studied by Abramov [10]. He showed that this reaction proceeds with evolution of heat in accordance with the equation

$$RCHO + HPO(OR')_2 \xrightarrow{R'ONa} R\cdot CH(OH)\cdot PO(OR')_2.$$

In our case ammonia evidently plays the part of basic catalyst:

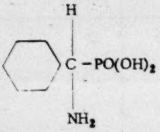
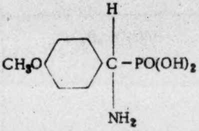
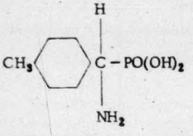
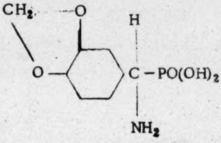
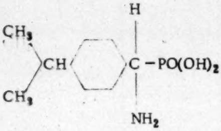
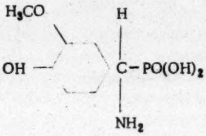
$$RCHO + HPO(OR')_2 \xrightarrow{NH_3} RCH(OH)PO(OR')_2.$$

It was quite natural to suppose that hydroxyalkylphosphonic esters were formed as intermediate products in our synthesis of aminoalkylphosphonic esters, and that the second stage, which occurred when the mixture was heated, was the substitution reaction

$$RCH(OH)PO(OR')_2 + NH_3 \rightarrow RCH(NH_2)PO(OR')_2 + H_2O.$$

Such a supposition, however, is in conflict with the results of Fields [9], who in a discussion of the mechanism of the reaction of amines with aldehydes and dialkyl hydrogen phosphites states that hydroxyalkylphosphonic

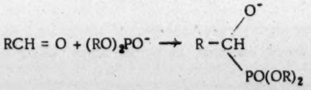
TABLE 2

1-Aminoalkylphosphonic acid	M.p. (°C)	Yield (%)	1-Aminoalkylphosphonic acid	M.p. (°C)	Yield (%)
	273	72		268-269	85
	276	81		255	35
	287	60		215	81

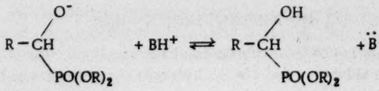
acids do not react at all with amines at low temperatures (56.118°), whereas at high temperatures (175°) complete resinification of the reaction mixture occurs. For this reason we carried out our first experiments on the conversion of hydroxyalkylphosphonic acids into aminoalkylphosphonic acids in presence of sodium ethoxide as catalyst, and replacement of hydroxyl by amino was actually found to occur. It therefore appeared to be possible to synthesize the aminoalkylphosphonic acid as follows: first obtain dialkyl α-hydroxybenzylphosphonate from benzaldehyde and dialkyl hydrogen phosphite under Abramov's conditions, and then, without separating this from the reaction mixture, add an alcoholic solution of ammonia and heat in a sealed tube to convert the hydroxy ester into the amino ester. We did, in fact, carry out the synthesis of α-aminobenzylphosphonic acid by this method, but we later found that the use of a catalyst was unnecessary. As we have already mentioned, the formation of the ester of the hydroxy acid occurs readily in the cold in presence of ammonia. The second stage of the synthesis, replacement of hydroxyl by amino, occurs when the hydroxy ester is simply heated with alcoholic ammonia in a sealed tube to 100°.

These experiments reveal the mechanism of the formation of an aminoalkylphosphonic ester by the heating of benzaldehyde with a dialkyl hydrogen phosphite and alcoholic ammonia. It may be supposed that at first the most rapid reaction is the addition of the dialkyl hydrogen phosphite to the aldehyde under the catalytic action of ammonia, a hydroxybenzylphosphonic ester being formed. When this ester is heated with ammonia, hydroxyl is replaced by amino, and an aminobenzylphosphonic ester is formed. The whole process may be represented by the following equations ($B = NH_3$ or RO^-):

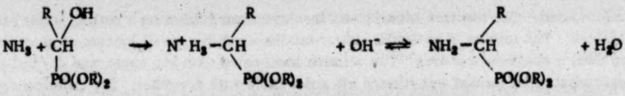
$$(RO)_2POH + \ddot{B} \rightleftharpoons (RO)_2PO^- + BH^+ \qquad \text{(I)}$$



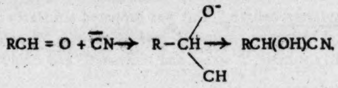
$$RCH=O + (RO)_2PO^- \rightarrow R-CH(O^-)PO(OR)_2$$



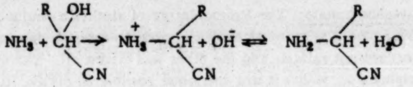
$$R-CH(O^-)PO(OR)_2 + BH^+ \rightleftharpoons R-CH(OH)PO(OR)_2 + \ddot{B}$$

 (II)

It is natural to compare the formation of aminoalkylphosphonic esters from aldehydes, ammonia, and dialkyl hydrogen phosphites with the well-known Zelinsky reaction, the formation of amino nitriles by the action of ammonium cyanide on aldehydes [11]. Here again we have a nucleophilic reagent, hydrocyanic acid, adding to a carbonyl group, and we have, in absence of ammonia:



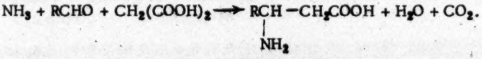
In presence of ammonia, however, not hydroxy nitriles, but amino nitriles are formed:



It is known also that isolated hydroxy nitriles can be converted into amino nitriles by the action of alcoholic ammonia [12]:

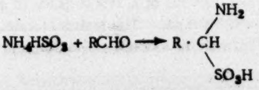
$$RCH(OH)CN + NH_3 = RCH(NH_2)CN + H_2O.$$

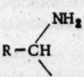
To the same type of reactions belongs, evidently, also Rodionov's reaction [13], in which the simultaneous action of ammonia and malonic acid on aldehydes leads to the formation of β-amino carboxylic acids:



$$NH_3 + RCHO + CH_2(COOH)_2 \longrightarrow \underset{\displaystyle NH_2}{\underset{|}{RCH}}-CH_2COOH + H_2O + CO_2.$$

In a similar way, ammonium bisulfite adds to aldehydes with formation of α-amino sulfonic acids [14]:



Dialkyl hydrogen phosphites in many of their reactions are reminiscent on the one hand of β-dicarbonyl compounds (malonic and acetoacetic esters) – an analogy which was examined systematically by Arbuzov [15] – and on the other hand of substances such as hydrocyanic and sulfurous acids, the diad tautomerism of which has been the subject of long discussions. In both cases, however, there is the possibility of obtaining two series of derivatives of the diad types. We may consider, on the basis of these comparisons, that the formation of α-amino-substituted derivatives of the type  by the action of aldehydes and ammonia is a general reaction for all substances HX that are weak acids and are able to show dual reactivity of the diad or triad type.

EXPERIMENTAL

Hydrochloride of Diethyl α-Aminobenzylphosphonate. A mixture of 6 g of benzaldehyde, 8 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The reaction mixture was then evaporated down on a boiling water bath until a constant residue was obtained. The residue, a yellowish sirup, was dissolved in a small amount of absolute ethanol, and dry ether was added until a turbidity appeared. The solution was cooled with ice water, and dry hydrogen chloride was passed. The precipitate that formed was filtered off and washed with dry ether. The colorless crystals obtained were readily soluble in water, methanol, and ethanol, and insoluble in benzene, acetone, and ether. The substance was crystallized from dioxane in the form of fine colorless needles, and these melted with decomposition at 158-159°. The yield was 6 g (38%).

Found %: N 5.0; 4.9; P 11.0; 11.1; Cl 12.3; 12.4
$C_{11}H_{19}NPO_3Cl$. Calculated %: N 5.0; P 11.1; Cl 12.7

Hydrochloride of Dibutyl α-Aminobenzylphosphonate. This was prepared similarly to the preceding substance from 10.6 g of benzaldehyde, 19.4 g of dibutyl hydrogen phosphite, and 40 ml of a 7% solution of ammonia in absolute butyl alcohol. The substance was readily soluble in water and methanol, and could be crystallized from ethanol or dioxane; m.p. 149°; yield 6.7 g (20%).

Found %: C 53.2; 53.2; H 7.8; 8.1; N 4.4; 4.1; P 9.1; 9.0
$C_{15}H_{25}NPO_3Cl$. Calculated %: C 53.7; H 8.1; N 4.2; P 9.3

Picrate of Diethyl α-Aminobenzylphosphonate. The hydrochloride of diethyl α-aminobenzylphosphonate (3.5 g; m.p. 155°) was treated with a 3% aqueous solution of $NaHCO_3$, and the solution obtained was extracted with ether. The ether solution was dried over sodium sulfate, and the ether was driven off. The residue was a yellowish oily liquid (diethyl α-aminobenzylphosphonate), which it was not found possible to purify. It was dissolved in dry ether, and an ethereal solution of picric acid was added. A yellow crystalline precipitate, m.p. 174°, was obtained.

Found %: N (in NH_2) 2.7; 2.6; P 6.9; 6.6
$C_{17}H_{21}N_4PO_{10}$. Calculated %: N 3.0; P 6.6

α-Aminobenzylphosphonic Acid. A mixture of 2 g of the hydrochloride of diethyl α-aminobenzylphosphonate and 50 ml of hydrochloric acid (1 : 1) was heated in a sealed tube at 120-140° for three hours. The reaction mixture was evaporated down on a boiling water bath until the odor of hydrochloric acid disappeared. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 0.9 g (72%) of a colorless crystalline substance, m.p. 272-273°.

Found %: C 45.4; 45.5; H. 5.3; 5.4; N 7.9; 7.7; P 16.6; 16.7
$C_7H_{10}PNO_3$. Calculated %: C 44.9; H 5.4; N 7.5; P 16.6

Hydrochloride of Diethyl α-Amino-p-methylbenzylphosphonate. This was prepared from 5.5 g of p-tolualdehyde, 6.5 g of diethyl hydrogen phosphite, and 13.5 ml of a 10% solution of ammonia in absolute ethanol, the procedure being as in the experiment with benzaldehyde The hydrochloride, which was precipitated with ether, was recrystallized after five days from a mixture of alcohol and ether, and yielded 1.1 g (8%) of product, which melted with decomposition at 148°.

Found %: C 49.4; 49.1; H 7.4; 7.3; N 4.9; 4.8; P 10.7; 10.8
$C_{12}H_{21}NPClO_3$. Calculated %: C 49.1; H 7.2; N 4.8; P 10.6

Picrate of Diethyl α-Amino-p-methylbenzylphosphonate. A mixture of 6 g of p-tolualdehyde, 7 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The reaction mixture was evaporated down on a boiling water bath, and the residue was extracted with ether. To the solution obtained an ethereal solution of picric acid was added, and the crystals that were precipitated were filtered off (3.95 g, i.e., 16%). The substance, after recrystallization from ethanol, melted with decomposition at 187°.

Found %: C 44.1; 44.3; H 5.2; 5.0; N (in NH_2) 2.8; 2.7; P 6.6; 6.5
$C_{18}H_{23}N_4PO_{10}$. Calculated %: C 44.4; H 4.8; N 2.9; P 6.4

α-Amino-p-methylbenzylphosphonic Acid. *A.* A mixture of 3.2 g of the picrate of diethyl α-amino-p-methylbenzylphosphonate and hydrochloric acid (1 : 1; 60 ml) was heated in sealed tubes at 110-120° for three hours. The reaction mixture was extracted with ether, and the aqueous solution was evaporated down. The residue was recrystallized from water, and yielded 0.5 g of product, m.p. 276°.

Found %: C 48.2; 48.3; H 5.8; 6.0; N 6.8; 6.7; P 15.5; 15.5
$C_8H_{12}NPO_3$. Calculated %: C 47.8; H 6.0; N 7.0; P 15.4

B. A mixture of 0.9 g of the hydrochloride of diethyl α-amino-p-methylbenzylphosphonate and 25 ml of hydrochloric acid (1 : 1) was heated in a sealed tube at 110° for three hours. The contents of the tube were evaporated down, and the residue was recrystallized from water, yielding 0.5 g (81%) of product, m.p. 276°.

Hydrochloride of Diethyl α-Amino-p-isopropylbenzylphosphonate. This was prepared from 7.4 g of p-isopropylbenzaldehyde, 8.3 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol, the procedure being as in the experiment with benzaldehyde. The product was recrystallized from absolute ethanol, and yielded 5.6 g (35%) of colorless crystals, melting with decomposition at 167°.

Found %: N 4.4; 4.5; P 9.4; 9.5

$C_{14}H_{25}NPClO_3$. Calculated %: N 4.4; P 9.6;

α-Amino-p-isopropylbenzylphosphonic Acid. This was prepared from 4.5 g of the hydrochloride of diethyl α-amino-p-isopropylbenzylphosphonate and 50 ml of hydrochloric acid (1 : 1) by heating them together in sealed tubes at 110-120° for three hours. After the evaporation, the residue was recrystallized from water, yielding 1.9 g (60%) of a colorless crystalline substance, which melted with decomposition at 267°.

Found %: C 52.5; 52.3; H 7.1; 6.9; N 6.1; 6.2; P 13.9; 13.8

$C_{10}H_{16}NPO_3$. Calculated %: C 52.4; H 7.0; N 6.1; P 13.5

Hydrochloride of Diethyl α-Amino-p-methoxybenzylphosphonate. This was prepared from 4.1 g of p-anisaldehyde, 4.15 g of diethyl hydrogen phosphite, and 7.5 ml of a 10% solution of ammonia in absolute ethanol. The substance was reprecipitated from a mixture of ether and alcohol, and 3 g (32%) of white crystals, m.p. 160°, was obtained.

Found %: C 46.9; 46.5; H 6.9; 6.9; Cl 11.6; 11.6; P.10.2; 10.3; N 4.2; 4.4

$C_{12}H_{21}NPO_4Cl$. Calculated %: C 46.7; H 6.8; Cl 11.5; P 10.2; N 4.5

α-Amino-p-methoxybenzylphosphonic Acid. A mixture of 1 g of the hydrochloride of diethyl α-amino-p-methoxybenzylphosphonate and 20 ml of hydrochloric acid (1 : 1) was heated in a sealed tube in a boiling water bath for six hours. Recrystallization from water yielded 0.55 g (85%) of a colorless crystalline substance, m.p. 278-279°.

Found %: N 6.2; 6.2; P 14.2; 14.5

$C_8H_{12}NPO_4$. Calculated %: N 6.4; P 14.3

Hydrochloride of Diethyl α-Amino-3,4-methylenedioxybenzylphosphonate. This was prepared from 4.5 g of piperonal, 4.2 g of diethyl hydrogen phosphite, and 20 ml of an ethanolic solution of ammonia. The product could be recrystallized from dioxane and reprecipitated from a mixture of alcohol and ether; it melted with decomposition at 145°. The yield was 4.2 g (43%).

Found %: C 44.3; 44.2; H 6.1; 6.2; N 4.4; 4.3; P 9.2; 9.4; Cl 10.3; 10.6

$C_{12}H_{19}NPO_5Cl$. Calculated %: C 44.5; H 5.9; N 4.3; P 9.6; Cl 10.9

Ethyl Hydrogen α-Amino-3,4-methylenedioxybenzylphosphonate. A mixture of 4.5 g of piperonal, 4.2 g of diethyl hydrogen phosphite, and 20 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes at 130-140° for five hours. The reaction mixture was evaporated down on a boiling water bath until a constant residue was obtained. The residue was transferred to some absolute ethanol, and the crystals remaining undissolved were filtered off and recrystallized from a mixture of water and alcohol. The product was 0.4 g (5%) of a water-soluble substance, m.p. 240°.

Found %: C 46.2; 46.3; H 5.9; 5.9; N 5.5; 5.4; P 11.9; 11.7

$C_{10}H_{14}NPO_5$. Calculated %: C 46.3; H 5.4; N 5.4; P 11.9

The alcoholic filtrate was saturated with dry hydrogen chloride and then treated exactly as in the preceding experiment. From the filtrate 0.3 g of ammonium chloride and 2.0 g (21%) of the hydrochloride of diethyl α-amino-3,4-methylenedioxybenzylphosphonate were isolated.

Hydrochloride of Dibutyl α-Amino-3,4-methylenedioxybenzylphosphonate. Prepared from 4.5 g piperonal, 5.8 g dibutyl hydrogen phosphite, and 10 ml of a 7% solution of ammonia in absolute butyl alcohol, the mixture being heated in sealed tubes in a boiling water bath for ten hours. The product was recrystallized from butyl alcohol, and 1.0 g (14%) was obtained of a substance that exhibited two melting points, 160° and 214°.

Found %: C 49.8; 50.7; H 7.4; 7.4; Cl 9.8; 9.6; P 8.4; 8.0; N 3.6; 3.6

$C_{16}H_{27}O_5PNCl$. Calculated %: C 50.6; H 7.1; Cl 9.4; P 8.2; N 3.7

α-Amino-3,4-methylenedioxybenzylphosphonic Acid. A mixture of 2 g of the hydrochloride of diethyl α-amino-3,4-methylenedioxybenzylphosphonate, m.p. 145°, and 40 ml of hydrochloric acid (1 : 1) was heated in a sealed tube in a boiling water bath for seven hours. The reaction mixture was evaporated down, and the residue was crystallized from water, yielding 0.5 g (35%) of a substance of m.p. 255°.

Found %: C 41.3; 41.3; H 4.5; 4.4; N 6.5; P 13.4; 13.5
$C_8H_{10}NPO_5$. Calculated %: C 41.5; H 4.3; N 6.1; P 13.4

Hydrochloride of Diethyl α-Amino-4-hydroxy-3-methoxybenzylphosphonate. This was prepared from 7.2 g of vanillin, 8.3 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol. Recrystallization of the product from absolute ethanol yielded 5 g (32%) of a substance that melted with decomposition at 181°.

Found %: C 44.4; 44.2; H 6.6; 6.8; P 9.8; 9.7; N 4.1; 4.2 Cl 10.8; 11.3
$C_{12}H_{21}NPClO_5$. Calculated %: C 44.2; H 6.5; P 9.5; N 4.3 Cl 10.9

α-Amino-4-hydroxy-3-methoxybenzylphosphonic Acid. This was prepared from 6 g of the hydrochloride of diethyl α-amino-4-hydroxy-3-methoxybenzylphosphonate and 120 ml of hydrochloric acid (1 : 1); the mixture being heated in sealed tubes in a boiling water bath for three hours. Recrystallization of the product from water yielded 3.5 g (81%) of substance of m.p. 215°.

Found %: N 6.0; 6.1; P 13.2; 13.1
$C_8H_{12}NPO_5$. Calculated %: N 6.0; P 13.3

Diethyl α-Hydroxybenzylphosphonate. A mixture of 6 g benzaldehyde, 8 g diethyl hydrogen phosphite, and 25 ml of a 10% solution of ammonia in absolute ethanol was sealed in tubes and set aside at room temperature for twelve days. The contents of the tubes were then evaporated down in a dish on a boiling water bath until a constant residue was obtained. On being cooled, the residue in the dish crystallized out, and the crystals obtained were washed with dry ether. The product was 5.9 g (43%) of a white crystalline substance, which melted, after recrystallization from petroleum ether, at 83-84°. In admixture with the diethyl α-hydroxybenzylphosphonate obtained by Kabachnik and Rossyskaya [6] it showed no depression of melting point.

Found %: C 54.5; 54.3; H 7.1; 7.2; P 12.9; 13.0
$C_{11}H_{17}PO_4$. Calculated %: C 54.1; H 7.0; P 12.7

The ether filtrate was saturated with dry hydrogen chloride, and the precipitated substance was filtered off, yielding 2.0 g (12%) of the hydrochloride of diethyl α-aminobenzylphosphonate.

Reaction of Diethyl α-Hydroxybenzylphosphonate with Ammonia (in Presence of Sodium Ethoxide). A mixture of 2.44 g of diethyl α-hydroxybenzylphosphonate (m.p. 82-83°), 3 ml of a 10% solution of ammonia in absolute ethanol, and a solution of 0.023 g of sodium in 2 ml of ethanol was heated in a sealed tube in a boiling water bath for seven hours. The substance obtained was reprecipitated from a mixture of alcohol and ether. The product (0.7 g, i.e., 25%) melted at 159°.

Found %: N 4.9; P 10.8; 10.6
$C_{11}H_{19}NPO_3Cl$. Calculated %: N 5.0; P 11.1

Reaction of Diethyl α-Hydroxybenzylphosphonate with Ammonia (in Absence of Catalyst). A mixture of 4.88 g of diethyl α-hydroxybenzylphosphonate and 6 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for seven hours. Recrystallization of the product from dioxane, yielded 1.5 g (27%) of a substance of m.p. 158°.

Found %: N 4.8; 5.0
$C_{11}H_{19}NPO_3Cl$. Calculated %: N 5.0

Preparation of the Hydrochloride of Diethyl α-Aminobenzylphosphonate via Diethyl α-Hydroxybenzylphosphonate. Sodium methoxide (20 drops) was added to a mixture of 5 g of benzaldehyde and 6.9 g of diethyl hydrogen phosphite, and the temperature of the mixture rose to 50°. The mixture was then heated in a boiling water bath for 30 minutes, and cooled. An addition was made of 15 ml of a 10% solution of ammonia in absolute ethanol, and the mixture was heated in sealed tubes in a boiling water bath for seven hours. The further treatment of the reaction mixture was carried out in the manner described for the experiment on the reaction of diethyl α-hydroxyphosphonate with ammonia. The product was 4 g (30%) of the hydrochloride of diethyl α-aminobenzylphosphonate, m.p. 155°.

SUMMARY

1. The reaction of aldehydes with dialkyl hydrogen phosphites and ammonia has been investigated, and it has been established that when heat is applied α-aminoalkylphosphonic esters are formed; on hydrolysis these yield the free acids.

2. By this method α-amino phosphonic acids have been synthesized from benzaldehyde, p-tolualdehyde, p-isopropylbenzaldehyde, p-anisaldehyde, piperonal, and vanillin.

3. It has been shown that benzaldehyde reacts with dialkyl hydrogen phosphites and ammonia in the cold with formation of α-hydroxybenzylphosphonic esters, which, on being heated with ammonia, are converted into α-aminobenzylphosphonic esters.

4. A mechanism has been proposed for the reaction, in which α-hydroxyalkylphosphonic esters play the part of intermediate products. A parallel has been drawn between the reaction observed and other reactions: Zelinsky's reaction, Rodionov's reaction, and the formation of α-amino sulfonic acids from aldehydes and ammonium bisulfite.

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HIGH-TEMPERATURE CONTACT-CATALYSIS REACTIONS OF NORMAL ALKANES IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov

We have previously studied contact-catalysis reactions of cyclopentanes and cycloalkanes under conditions of high temperature and pressure [1]. It was then shown that at 460° under a hydrogen pressure of 15-20 atm, cyclopentane, methycyclopentane, and cyclohexane underwent a number of far-reaching changes in presence of a platinized alumina catalyst, the products being aromatic hydrocarbons, alkylation and isomerization products, and a considerable amount of paraffins of normal and branched structures.

It was considered to be of interest to examine the transformations, under the same conditions, of normal alkanes (hexane, heptane, and octane). In these experiments it was proposed to obtain data that would permit a comparative examination of the behavior of these normal alkanes in its relation to their molecular weights, and would enable the mechanism of the formation of branched paraffins and aromatic hydrocarbons under the given conditions to be elucidated.

EXPERIMENTAL

The hexane, heptane, and octane taken for the investigation were obtained by dehydration of the corresponding primary alcohols at 360° in presence of alumina, followed by hydrogenation of the alkenes obtained in presence of a nickel catalyst. The hydrocarbons were purified by careful distillation through a 35-plate column.

Catalytic Treatment of Hexane

The hexane used had the following properties: b.p. 68.8° (750 mm); n_D^{20} 1.3765; d_4^{20} 0.6697; Found MR_D 29.97; Calculated MR_D for C_6H_{14} 30.21.

This hydrocarbon (780 ml, i.e., 514.6 g) was passed at 460° over a platinized alumina catalyst at a space velocity of 0.43 under a pressure of 20 atm of hydrogen. As a result 355.3 g (528.6 ml) of catalyzate was obtained; it boiled over the range 27.5-87°, had n_D^{20} 1.3840; d_4^{20} 0.6721, and contained 7% of aromatic hydrocarbons. The yield was 69% on the amount of hexane taken.

Distillation of 35.6 g of the catalyzate over sodium through a column yielded a residue of 0.65 g, which boiled over the range 87-153° at 749 mm. This residue was subjected to Ullmann permanganate oxidation, and from the resulting mixture [2], 0.0097 g of pure benzoic acid, m.p. 121.6° and 0.1505 g of a mixture of benzenedicarboxylic acids, m.p. 290-292°, were isolated. In order to avoid loss of the highly volatile components of the catalyzate, the remaining bulk of it was fractionated through a 70-plate column in order to obtain the hydrocarbons boiling up to 38° at 752 mm, and the following fractions were obtained:

Fraction I, b.p. 27-28.0°; 10.5 ml (6.5 g); n_D^{20} 1.3545; d_4^{20} 0.6203
Fraction II, b.p. 35-35.6°; 12 ml (7.5 g); n_D^{20} 1.3570; d_4^{20} 0.6278

Comparison of the properties of these fractions with data in the literature for 2-methylbutane and pentane showed that they consisted, respectively, of these hydrocarbons.

After the isopentane and pentane had been removed from the catalyzate, aromatic hydrocarbons were removed by treatment with 3% oleum; the catalyzate residue then had n_D^{20} 1.3760; and d_4^{20} 0.6586. For fractionation through the 70-plate column, 125.6 g (190.6 ml) of the catalyzate was taken, and the results of the fractionation are presented in Table 1 and Fig. 1. The gas that was isolated in the various trials contained from 78 to 86% of hydrogen, the remainder being saturated hydrocarbons; for example, the analysis of the gas from Trial No. 7 was: 79.2% of hydrogen, 20.8% of saturated hydrocarbons.

TABLE 1

Fractional Composition of the Paraffin Part of the Hexane Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)		
					on catalyzate	on hexane taken	on mixture of alkanes taken for fractionation
I	48.5-50.5	3.6	1.3670	0.6478	1.5	1.0	2.8
II	50.5-59.5	21.8	1.3715	0.6526	15.6	10.7	17.3
III	59.5-61.5	16.0	1.3710	0.6532	11.5	7.9	12.7
IV	61.5 63.0	1.4	1.3760	—	0.7	0.5	1.1
V	63.0-64.0	19.9	1.3760	0.6641	14.0	9.7	15.8
VI	64.0-68.5	2.0	1.3760	—	0.8	0.5	1.6
VII	68.5	53.4	1.3765	0.6590	38.7	26.7	42.5
	Residue	6.6	1.3765	0.6597	5.1	3.5	5.3

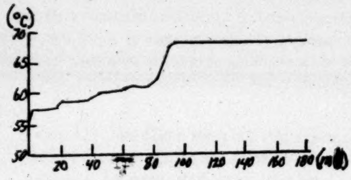
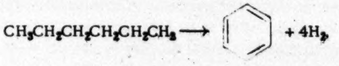


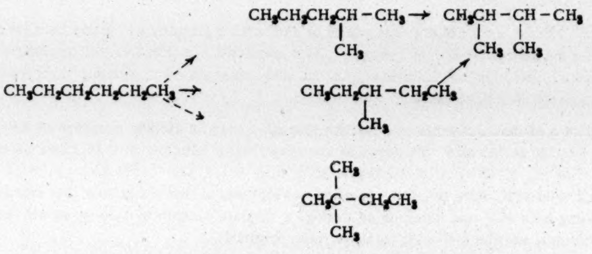
Fig. 1. Fractionation curve for the paraffin part of the hexane catalyzate.

Comparison of the properties of Fraction I of the paraffin part of the catalyzate with data in the literature for 2,2-dimethylbutane showed that it consisted mainly of this hydrocarbon. It was evident from an examination of the properties of Fraction II that it consisted mainly of 2,3-dimethylbutane, and optical analysis of it showed* that it contained 95% of 2,3-dimethylbutane and about 5% of 2,2-dimethylbutane. Fractions III, IV, and V consisted of mixtures of 2- and 3-methylpentane. Fraction VII was unchanged hexane.

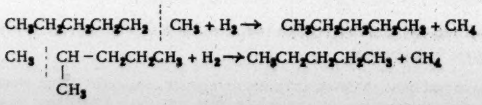
Under these conditions, therefore, hexane undergoes the following transformations: part of it (about 10%) is converted as a result of dehydrocyclization into benzene:



and the main bulk of it isomerizes into branched hexane isomers (2- and 3-methylpentanes, 2,3- and 2,2-dimethylbutanes):



At the same time hydrogenolysis reactions occur with formation of pentane:



$$CH_3CH_2CH_2CH_2CH_2 \,\vdots\, CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 + CH_4$$

$$CH_3 \,\vdots\, \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2CH_2CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 + CH_4$$

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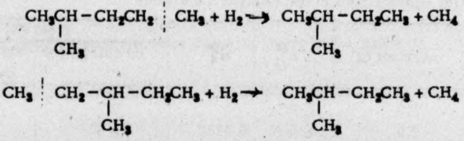
* Optical analyses were carried out on 12 fractions of the catalyzates from the three investigated alkanes by M. I. Batuev, to whom we express our thanks.

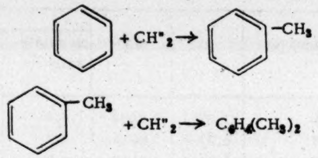
and 2-methylbutane:



$$\underset{\displaystyle CH_3}{CH_3CH}-CH_2CH_2 \;\vdots\; CH_3 + H_2 \rightarrow \underset{\displaystyle CH_3}{CH_3CH}-CH_2CH_3 + CH_4$$

$$CH_3 \;\vdots\; CH_2-\underset{\displaystyle CH_3}{CH}-CH_2CH_3 + H_2 \rightarrow \underset{\displaystyle CH_3}{CH_3CH}-CH_2CH_3 + CH_4$$

A considerable amount (about 30%) of the substance (the original hexane and its transformation products) undergoes cracking with formation of gaseous alkanes. The formation of small amounts of toluene and xylenes shows that, in this case also, the breakdown of hydrocarbons (hexane, the products of its isomerization and hydrogenolysis, and cyclohexane formed intermediately by the dehydrocyclization of hexane) is accompanied by the formation of methylene radicals, most of which are hydrogenated to methane $CH''_2 + H_2 \rightarrow CH_4$, while the remainder methylate benzene:



The results obtained show that the main direction in the contact-catalysis reactions of hexane under the conditions investigated is its isomerization into the corresponding branched paraffins having one or two tertiary carbon atoms. 2,2-Dimethylbutane is formed only to a slight extent. Also, dehydrocyclization occurs to an appreciable extent.

Catalytic Treatment of Heptane

The transformations of heptane b.p. 98.3° (751 mm); n_D^{20} 1.3876; d_4^{20} 0.6829) were studied in presence of the same catalyst at 460° under an excess pressure of hydrogen of 15 atm. For the catalytic reaction, 800 ml (546.3 g) of heptane was taken, and it was passed through the catalysis tube at a space velocity of 0.43. The catalyzate (501.7 ml, i.e., 345.9 g) had n_D^{20} 1.4035; d_4^{20} 0.6895, and contained 18% by volume of aromatic hydrocarbons. The yield was 63.3%. As in the case of hexane, before separation of aromatic hydrocarbons, 2-methylbutane and pentane were removed from the catalyzate through a 70-plate column. These hydrocarbons had the following properties: 2-methylbutane, b.p. 27.6-28° (742 mm), n_D^{20} 1.3536; d_4^{20} 0.6201; pentane, b.p. 35-35.6° (742 mm), n_D^{20} 1.3575; d_4^{20} 0.6280.

The aromatic hydrocarbons were separated from the catalyzate by the chromatographic method. For the adsorption, 285 ml (196.5 g) of catalyzate freed from 2-methylbutane and pentane was taken, and the aromatic hydrocarbons separated (56.0 ml, i.e., 48.4 g) had n_D^{20} 1.4980 and d_4^{20} 0.8654. They were fractionated through a 35-plate column, with the results shown in Table 2.

Ullmann oxidation of the toluene-xylene fraction (V, 110.5-138°) yielded 2.4 g of a mixture of carboxylic acids, from which, apart from a trace of benzoic acid, the following acids were isolated: 0.6071 g of phthalic acid (converted into phthalic anhydride, m.p. 130.8°), 1.2740 g of isophthalic acid (converted into the dimethyl ester, m.p. 66.8°), and 0.3085 g of terephthalic acid (identified via the dimethyl ester, m.p. 140°). The residue (6.4 g) (n_D^{20} 1.5480) was distilled from a flask having a Vigreux column; at 752 mm it distilled over a wide range of temperature (150-243°).

It follows from the results given in Table 2 that the aromatic part of the heptane catalyzate contained, in addition to toluene (69.8%), appreciable amounts of benzene, xylenes, and also, in the residue, evidently polymethylbenzenes. It is possible that the presence of xylene and polymethylbenzenes resulted from the methylation of benzene by methylene radicals formed under our experimental conditions.

The paraffin part of the catalyzate (228.5 ml, i.e., 155.1 g; n_D^{20} 1.3895 and d_4^{20} 0.6787) was subjected to precise fractionation through a 70-plate column. The results of the fractionation and the properties of the fractions collected are shown in Table 3 and Fig. 2.

TABLE 2
Fractional Composition of Aromatic Hydrocarbons in the Heptane Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)	
					on catalyzate	on mixture of aromatic hydrocarbons taken
I	to 80.0	1.3	1.4960	–	0.7	2.6
II	80.0-80.5	2.0	1.4995	0.8782	1.0	4.0
III	80.5-109.8	1.4	1.4970	–	0.7	2.8
IV	109.8-110.5	33.8	1.4965	0.8670	17.2	69.8
V	110.5-138	3.0	1.4970	0.8650	1.5	6.2
	Residue	6.4	1.5480	–	3.3	13.1

TABLE 3
Fractional Composition of the Paraffin Part of the Heptane Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)		
					on catalyzate	on heptane taken	on mixtures of alkanes taken for fractionation
I	46.5-59.5	7.9	1.3721	0.6580	4.3	2.9	5.1
II	59.5-76.0	6.7	1.3765	0.6615	4.2	2.8	4.3
III	76.0-87.0	8.6	1.3860	0.6617	4.6	3.1	5.4
IV	87.0-89.5	16.6	1.3890	0.6795	8.7	5.9	10.7
V	89.5-91.5	24.5	1.3890	0.6929	12.9	8.8	15.5
VI	91.5-92.0	17.7	1.3880	0.6875	9.2	6.3	11.4
VII	92.0-97.5	22.4	1.3880	0.6881	11.5	6.9	14.4
VIII	97.5-98.8	34.5	1.3876	0.6841	17.9	12.2	21.2
	Residue	9.6	1.3880	0.6843	4.9	3.4	6.2

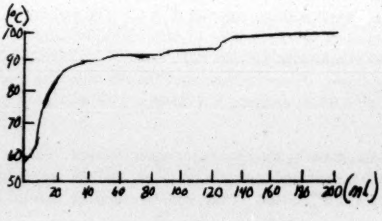


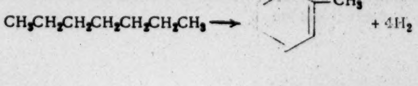
Fig. 2. Fractionation curve for the paraffin part of the heptane catalyzate.

The results of the fractionation of the paraffin part of the heptane catalyzate and comparisons of the properties of the fractions with those of individual hydrocarbons show that the transformations of heptane are similar to those of hexane: in this case the main reactions are isomerization to 2- and 3-methylhexanes, fission reactions, and aromatization. Comparison of the properties of Fraction I with the data in the literature for 2,2-dimethylbutane indicates that this hydrocarbon forms the bulk of the fraction.

Fraction II and united Fractions III and IV were investigated by the Raman spectrum method, and this indicated that Fraction II contained 55% of 2-methylpentane and 45% of 2,2-dimethylpentane, and that united Fractions III and IV contained 48% of 2,2-dimethylpentane and 52% of 2,4-dimethylpentane. The properties of Fraction V indicated it was a mixture of 3,3- and 2,3-dimethylpentanes; Fractions VI and VII consisted mainly of 2- and 3-methylhexanes; and Fraction VIII contained unchanged heptane.

Analysis of the gas evolved showed that it contained a rather higher amount of saturated hydrocarbons than the gas obtained from hexane. Thus, in various trials the saturated-hydrocarbon content varied from 22 to 25%.

The investigation of the heptane catalyzate showed that, in presence of a platinized alumina catalyst at 460° under 15 atm of hydrogen, part of the original hydrocarbon underwent dehydrocyclization with formation of toluene:



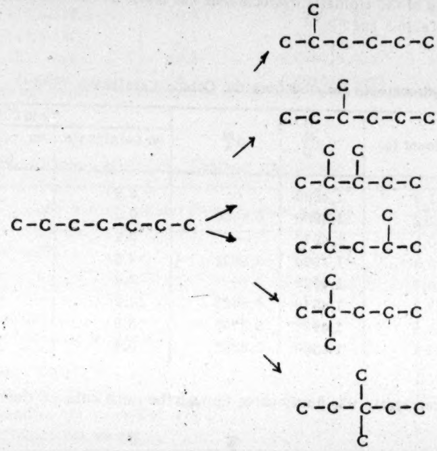
The observed formation of xylenes and more complex benzene homologs is evidently to be explained in this case also by the methylation of toluene by methylene radicals that are formed under our experimental conditions.

Many of these radicals are converted into methane: $CH_2^{\cdot\cdot} + H_2 \rightarrow CH_4$, and the remainder react with toluene with formation of xylenes and more complex methylation products:

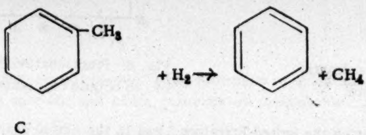
$$C_6H_5-CH_3 + CH_2^{\cdot\cdot} \rightarrow C_6H_4(CH_3)_2;$$

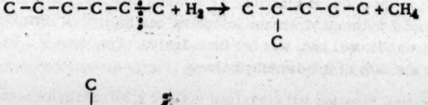
$$C_6H_4(CH_3)_2 + nCH_2^{\cdot\cdot} \rightarrow C_6H_{4-n}(CH_3)_{n+2}.$$

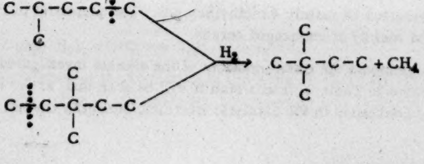
The results of the contact-catalysis transformations of hexane and heptane show that methylene radicals arise not only as a result of the fission of cycloalkanes (which are formed, in this case, only intermediately), but also in the methane breakdown of alkanes. The greater part of the heptane undergoes isomerization with formation of 2- and 3-methylhexanes and 2,3-, 2,4-, 2,2-, and 3,3-dimethylpentanes:



In addition to dehydrocyclization, methylation, and isomerization, hydrogenolysis occurs also, both of the paraffins and of the benzene homologs:







Catalytic Treatment of Octane

The experiments were carried out with 850 ml (597.8 g) of octane having the following constants: n_D^{20} 1.3980; d_4^{20} 0.7033, b.p. 125-126° (753 mm); Found MR_D 39.30, Calculated C_8H_{18} for MR_D 39.14. The catalytic treatment was carried out under the same conditions as those of the heptane experiments, and 492.3 ml (381.5 g, i.e., 63.8%) of catalyzate was obtained; it had the boiling range 27-159°, had n_D^{20} 1.4260; d_4^{20} 0.7748, and contained 32% of aromatic hydrocarbons. In the same way as in the previous experiments, fractions boiling up to 37° at 758 mm were distilled off:

Fraction I, b.p. 27.5-28°; 14.5 ml (9.1 g); n_D^{20} 1.3545; d_4^{20} 0.6201 (yield on octane taken 1.5%)
Fraction II, b.p. 28-35.5°; 0.1 ml
Fraction III, b.p. 35.5-37°; 16 ml (10.0 g); n_D^{20} 1.3576; d_4^{20} 0.273; yield 1.7.

By adsorption of silica gel 86.1 ml (73.8 g) of aromatic hydrocarbons of n_D^{20} 1.4975 and d_4^{20} 0.8673 was isolated from 290 ml (229.1 g) of catalyzate freed from highly volatile components. It was fractionated through a 70-plate column (73.6 ml, i.e., 63.0 g of the aromatic hydrocarbons was taken for the fractionation). The results of the fractionation are shown in Table 4 and Fig. 3.

TABLE 4
Fractional Composition of Aromatic Hydrocarbons Isolated from the Octane Catalyzate.

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)	
					on catalyzate	on mixture taken for fractionation
I	to 79.5	1.7	1.4860	—	0.9	2.7
II	79.5-80.3	1.2	1.4980	0.8780	0.6	1.2
III	80.3-109.8	0.5	1.4970	—	0.2	0.9
IV	109.8-110.5	5.6	1.4960	0.8672	2.6	8.8
V	110.5-137.6	0.7	1.4965	—	0.3	1.1
VI	137.6-138.6	27.8	1.4970	0.8625	14.2	44.1
VII	138.6-144.2	17.9	1.4997	0.8709	8.9	28.1
	Residue	7.1	1.5690	0.8892	3.4	11.3

The paraffin part of the octane catalyzate was fractionated through the same column; the results are presented in Table 5 and Fig. 4.

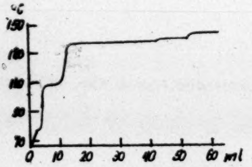


Fig. 3. Fractionation curve for the aromatic hydrocarbons of the octane catalyzate.

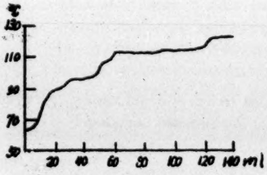


Fig. 4. Fractionation curve for the paraffin part of the octane catalyzate.

For Raman-spectrum investigation the united Fractions I and II, the united Fractions V and VI, and Fraction III were taken. The analysis showed that Fractions I + II contained about 60% of 2-methylpentane, 20% of hexane, and a certain amount of 2,2-dimethylpentane (detected qualitatively). Fraction III consisted mainly of heptane. Fraction IV, being a transitional one, was not investigated. Fractions V + VI consisted approximately of 70% of 2,4-dimethylhexane and 30% of 2,3-dimethylhexane.

According to their properties, Fraction VII contained mainly 2,3-dimethylhexane, Fraction VIII mainly 2-methylheptane, and Fraction IX mainly 4-methylheptane. The properties of Fraction X and of the residue indicated that they consisted mainly of unchanged octane.

It is of interest to compare the transformations of the alkanes investigated, and the material required for the comparison is presented in Table 6, from which it will be seen that, as the molecular weight of the alkane increases, the degree of conversion in the catalytic treatment rises; the amount of aromatic hydrocarbons formed also rises.

TABLE 5
Fractional Composition of the Paraffin Part of the Octane Catalyzate

Fraction No.	Boiling range (°C)	Amount(g)	n_D^{20}	d_4^{20}	Yield (%)		
					on catalyzate	on octane taken	on mixture of alkanes taken for fractionation
I	57.0-86.5	10.2	1.3890	0.6813	6.3	4.1	10.0
II	86.5-89.0	6.5	1.3825	0.6857	3.9	2.5	5.1
III	89.0-98.5	8.3	1 3880	0.6890	5.0	3.2	8.1
IV	98.5-106.5	8.2	1.3930	0.6935	5.0	3.2	8.0
V	106.5-110.5	15.2	1.3990	0.6975	9.1	5.9	14.8
VI	110.5-115.5	16.0	1.3995	0.7126	9.5	6.2	15.7
VII	115.5-117.5	5.1	1.4010	0.7106	3.0	1.9	5.0
VIII	117.5-118.5	10.7	1.4020	0.7020	6.5	4.2	10.5
IX	118.5-125.0	2.1	1.3980	0.7025	1.2	0.8	2.0
X	125 -126.0	10.5	1.3980	0.7031	6.3	4.1	10.3
	Residue	8.4	1.3980	0.7033	5.0	3.2	8.3

TABLE 6
Nature of the Transformations of Hexane, Heptane, and Octane

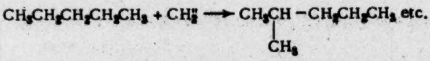
Transformation products (% on original alkane)	Alkane		
	Hexane	Heptane	Octane
Degree of conversion (%)	69.8	84.4	92.7
Gaseous products	31.0	31.5	34.7
Liquid catalyzate	69.0	63.3	63.8
Aromatic hydrocarbons	4.8	12.3	21.0
Branched paraffins (isomeric to alkane)	31.4	37.9	23.9
those having a tertiary C	28.8	30.0	19.0
those having a quaternary C	1.5	6.7	3.2
branched paraffins not accounted for	1.1	1.2	1.7
Paraffins of lower molecular weight	2.6	2.7	13.0
2-methylbutane	1.2	1.4	1.5
pentane	1.4	1.3	1.7
hexane and its isomers	–	–	6.6
heptane and its isomers	–	–	3.2
Unchanged alkane	30.2	15.6	7.3
Losses	1.0	–	–

Isomerization of the alkanes leads mainly to the formation of hydrocarbons having a tertiary carbon atom. Together with isomers having only one side chain, however, an appreciable amount of more highly branched paraffins is formed.

An examination of the chemical nature of the octane catalyzate gives us reason to suppose that, under the given conditions, the nature of the contact-catalysis reactions of this alkane is quite analogous to that of the various transformations of its homologs, heptane and hexane. In this case also, the reactions of dehydrocyclization, alkylation, isomerization, and hydrogenolysis are clearly manifest. The properties of the residue from the fractionation of the aromatic hydrocarbons formed (benzene, toluene, and xylenes) show that it consists of higher benzene homologs, arising by the methylation of xylenes with methylene radicals:

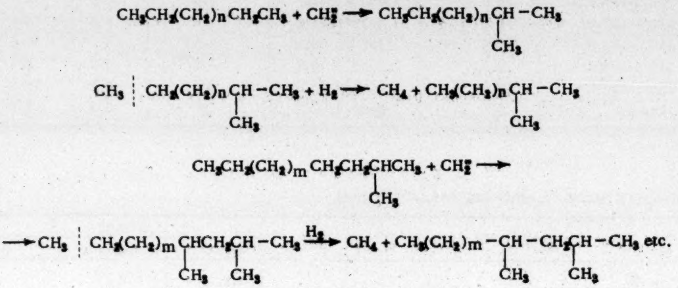
$$C_6H_4(CH_3)_2 + CH_2^{''} \longrightarrow C_6H_3(CH_3)_3 \text{ etc.}$$

The question arises of the mechanism of the formation of the isomeric paraffins. It is evident that in the catalytic treatment of alkanes, as also in that of cycloalkanes, an important part is played in their transformations by methylene breakdown of part of the substance, with subsequent methylation of alkanes by the methylene radicals formed, yielding branched hydrocarbons, e.g.:



$$CH_3CH_2CH_2CH_2CH_3 + CH_2^{:} \rightarrow CH_3\underset{\overset{|}{CH_3}}{CH} - CH_2CH_2CH_3 \text{ etc.}$$

This concept of ours on the ways in which branched paraffins are formed under the conditions of the contact-catalysis reactions of normal alkanes at high temperatures and at high pressures of hydrogen is based, as we have seen, on the synthetic process of alkylation by means of radicals; we are inclined to make this same concept the basis of our explanation of the mechanism of the isomerization of n-alkanes under these conditions, our scheme for the process, which consists of successive methylation and hydrogenolysis reactions, being as follows:



$$CH_3CH_2(CH_2)_nCH_2CH_3 + CH_2^{:} \rightarrow CH_3CH_2(CH_2)_n\underset{\overset{|}{CH_3}}{CH} - CH_3$$

$$CH_3 \,\vdots\, CH_2(CH_2)_n\underset{\overset{|}{CH_3}}{CH} - CH_3 + H_2 \rightarrow CH_4 + CH_3(CH_2)_n\underset{\overset{|}{CH_3}}{CH} - CH_3$$

$$CH_3CH_2(CH_2)_m CH_2CH_2\underset{\overset{|}{CH_3}}{CH}CH_3 + CH_2^{:} \rightarrow$$

$$\rightarrow CH_3 \,\vdots\, CH_2(CH_2)_m \underset{\overset{|}{CH_3}}{CH}CH_2\underset{\overset{|}{CH_3}}{CH} - CH_3 \xrightarrow{H_2} CH_4 + CH_3(CH_2)_m - \underset{\overset{|}{CH_3}}{CH} - CH_2\underset{\overset{|}{CH_3}}{CH} - CH_3 \text{ etc.}$$

SUMMARY

1. A study has been made of the contact-catalysis reactions of hexane, heptane, and octane in presence of platinized alumina at 460° under a high pressure of hydrogen (15-20 atm).

2. It has been shown that in all cases, under the given conditions, dehydrocyclization and isomerization of the alkanes occur, and both the alkanes themselves, and also benzene homologs formed as a result of catalytic dehydrocyclization, undergo methylation and hydrogenolysis.

3. It has been suggested that the methylene breakdown of alkanes and cycloalkanes plays a part in the formation of branched paraffins and higher benzene homologs.

4. A new concept has been advanced relating to the contact-catalysis isomerization reactions of alkanes at high temperatures in presence of hydrogen at high pressure.

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Institute of Organic Chemistry of the USSR Academy of Sciences

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[1] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 271 (1953).*

[2] B. L. Moldavsky, G. L. Kanusher, and M. V. Kobylskaya, J. Gen. Chem., 7, 167 (1937).

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*See Consultants Bureau, Page 243.

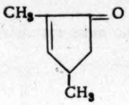
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVII. PREPARATION OF α,β-UNSATURATED CYCLIC KETONES (2-CYCLOALKEN-1-ONES)

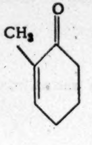
I. N. Nazarov, L. D. Bergelson, I. V. Torgov, and S. N. Ananchenko

In a series of communications [1] we have described numerous condensations of dienes with α,β-unsaturated cyclic ketones leading to the synthesis of various polycyclic compounds, including compounds related to steroids.

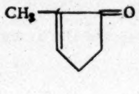
Among the unsaturated cyclic ketones employed in these condensations were: 2,4-dimethyl-2-cyclopenten-1-one (I), 2-methyl-2-cyclohexen-1-one (II), 2-methyl-2-cyclopenten-1-one (III), 2-cyclohexen-1-one (IV), and 2-cyclopenten-1-one (V).



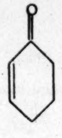
(I)



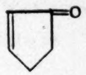
(II)



(III)



(IV)

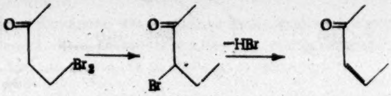


(V)

Although 2,4-dimethyl-2-cyclopenten-1-one (I) is simply prepared by the method discovered in our laboratory [2], which is based on the cyclization of allyl vinyl ketones, the preparation of the ketones II, III, IV, and V presents considerable difficulties.

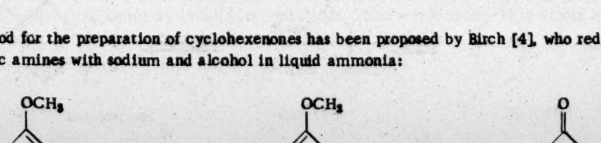
A review of the literature shows that no satisfactory method for the synthesis of α,β-unsaturated cyclic ketones exists, all the methods described for their preparation being complicated and giving poor yields.

Certain α,β-unsaturated ketones have been prepared by Koetz [3] from α-bromo or α-chloro ketones, with elimination of hydrogen bromide or chloride:

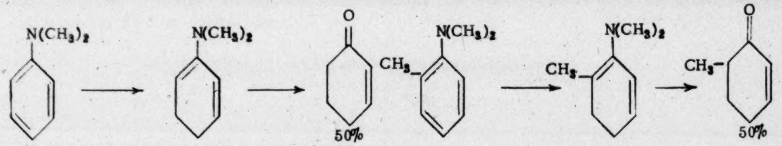


In spite of the commonplace character of this method, it has been studied rather superficially and has given very low yields of unsaturated ketones (5-8%). In the case of 2-cyclohexen-1-one, Koetz gives no indication at all of the yield.

An interesting method for the preparation of cyclohexenones has been proposed by Birch [4], who reduced phenol ethers and aromatic amines with sodium and alcohol in liquid ammonia:

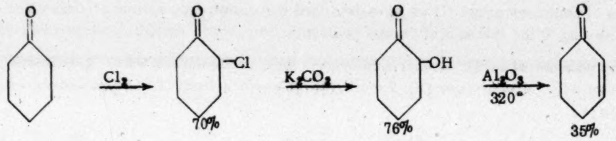


20%


N(CH$_3$)$_2$
N(CH$_3$)$_2$
O
CH$_3$
N(CH$_3$)$_2$
50%
N(CH$_3$)$_2$
CH$_3$
O
CH$_3$
50%

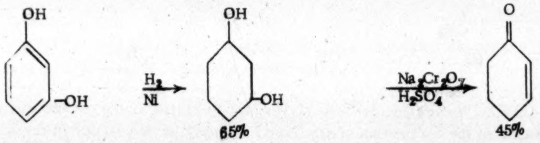
In all cases, however, the products included isomers having the double bond in another (nonconjugated) position, and this made the purification of the 2-cyclohexen-1-ones very difficult. This method is quite unsuitable for the preparation of 2-methyl-2-cyclohexen-1-one.

A relatively satisfactory method for the preparation of 2-cyclohexen-1-one was developed by Bartlett and Woods [5]:


O
Cl_2
O
Cl
70%
K_2CO_3
O
OH
76%
Al_2O_3
320°
O
35%

The overall yield was 18%.

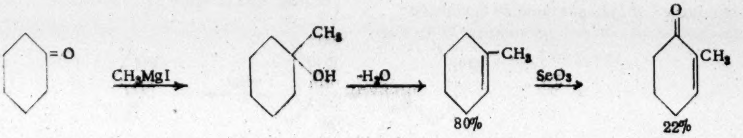
An original method has been proposed also by Rigby [6], who started from the more expensive resorcinol:


OH
OH
H_2
Ni
OH
OH
65%
$Na_2Cr_2O_7$
H_2SO_4
O
45%

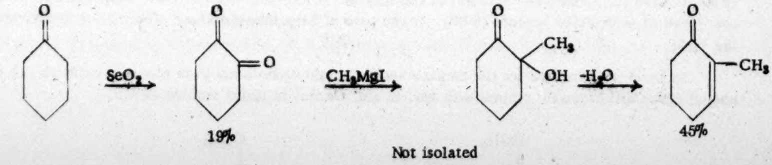
The overall yield was 29%.

Up to now no satisfactory method for the preparation of 2-methyl-2-cyclohexen-1-one has been given. Thus Buu [7] obtained it by the following two methods:

1.


=O
CH_3MgI
CH$_3$
OH
$-H_2O$
CH$_3$
80%
SeO_2
O
CH$_3$
22%

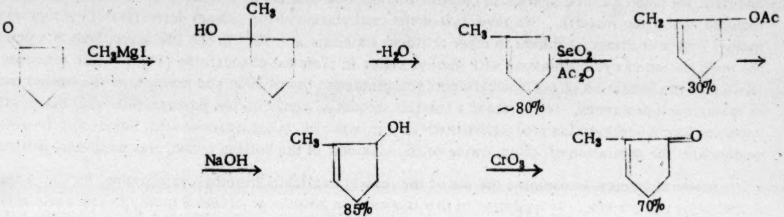
2.


O
SeO_2
O
=O
19%
CH_3MgI
O
CH$_3$
OH
$-H_2O$
Not isolated
O
CH$_3$
45%

The first method gave an overall yield of 18%, but after fractionation and purification analysis gave a low (by 2%) carbon content. The second method gave an overall yield of 9% of ketone, which again was not pure.

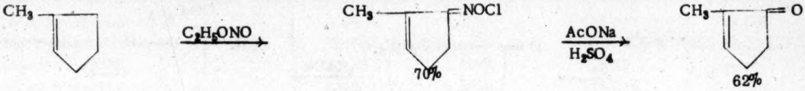
It is interesting to note that the method of brominating 2-methylcyclohexanone and then eliminating hydrogen bromide was not used, because Koetz has asserted [8] that the bromine attacks the unsubstituted methylene group, so that elimination of hydrogen bromide yields not 2-methyl- but 6-methyl-2-cyclohexen-1-one. As will be shown below, this assertion is incorrect, and the bromination of 2-methylcyclohexanone, as that of other 2-methylcycloalkanones, occurs only at the tertiary carbon atom. It was on account of the same preconceived idea that Mousseron [9], without any proof, ascribed the structure of 2-chloro-5-methylcyclopentanone to the chlorination product of 2-methylcyclopentanone.

2-Methyl-2-cyclopenten-1-one (III) was synthesized by Dane [10] as follows:



The yield was about 14% on the amount of cyclopentanone taken.

A simpler method was proposed by Rinkes [11]:



In this method the yield was 33% on the amount of cyclopentanone taken.

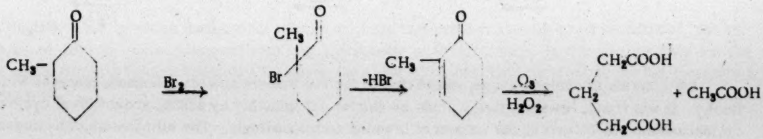
2-Cyclopenten-1-one (V) was prepared by Dane [12] in a similar manner, the overall yield being less than 5% on the amount of cyclopentene taken.

We have here cited methods that are the most acceptable with respect to the ultimate yield, and have omitted other syntheses, in which α,β-unsaturated cyclic ketones are obtained in insignificant yield [13, 14].

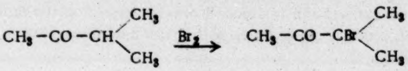
In this paper we give a general method for the preparation of α,β-unsaturated cyclic ketones: it is based on the bromination of saturated cyclic ketones and subsequent elimination of hydrogen bromide. We give also a simplified method for the preparation of 2,4-dimethyl-2-cyclopenten-1-one.

The bromination of 2-methylcyclohexanone was performed in an irradiated water-chloroform system at 30-35° in presence of calcium carbonate. At a lower temperature the reaction proceeds irregularly, and the yield is lower. Bromination by means of dioxane dibromide in ether gives worse results.

In the early experiments the bromo ketone was isolated by vacuum distillation, but it was later found to be more expedient to treat it immediately, without isolation, with diethylaniline. The elimination of hydrogen bromide was carried out at 100°, and the 2-methyl-2-cyclohexen-1-one formed was distilled off (58% yield). As the results of ozonization showed, none of the isomeric 6-methyl-2-cyclohexen-1-one was formed: only acetic and glutaric acids were isolated after ozonization; no methylglutaric acid was detected:



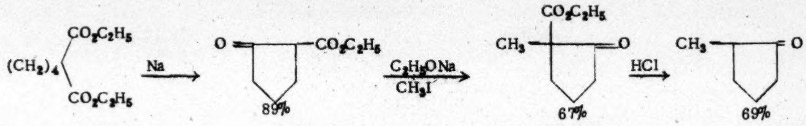
It has thus been proved beyond doubt that the bromination of 2-methylcyclohexanone occurs entirely at the tertiary carbon atom; this is in complete accord with A. E. Favorsky's results [15] on the bromination of 3-methyl-2-butanol, in which the bromine again reacts at the tertiary carbon atom:



$$CH_3-CO-CH\begin{matrix}CH_3\\ CH_3\end{matrix} \xrightarrow{Br_2} CH_3-CO-CBr\begin{matrix}CH_3\\ CH_3\end{matrix}$$

Before beginning work on the development of a method for the preparation of 2-methyl-2-cyclopenten-1-one (III), we made an investigation in order to find the best method of preparing the 2-methylcyclopentanone required as starting material. We investigated the methylation of the sodium derivative of cyclopentanone with methyl iodide or dimethyl sulfate in ether or liquid ammonia at −70°. In the literature there is a description of the methylation of cyclopentanone with methyl iodide in presence of sodamide [16], but side reactions occurred leading to the formation of cyclopentylidenecyclopentanone (up to 90%) and products of the further methylation of methylcyclopentanone. We obtained a smaller amount of condensation products (40-50%), but in all of the experiments the methylation product consisted of a mixture of cyclopentanone with mono- and di-methylcyclopentanones, the separation of which, owing to the closeness of the boiling points, was extremely difficult.

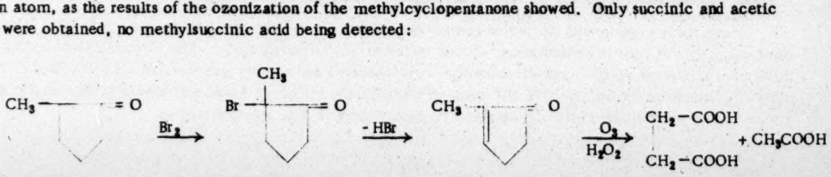
It was of interest to examine the use of the readily available 2-methylcyclohexanol for the preparation of 2-methylcyclopentanone. By oxidation of this it should be possible to obtain 2-methylhexanedioic acid (together with adipic acid), cyclization of which should yield the required ketone. Actually, oxidation of 2-methylcyclohexanol with nitric acid in presence of ammonium vanadate gave 2-methylhexanedioic acid in 70% yield. The cyclization of this, however, with the aid of baryta or acetic anhydride gave only 10-12% of 2-methylcyclopentanone. We therefore considered it more expedient to proceed by the usual method: the Dieckmann condensation of diethyl adipate, followed by methylation and decarboxylation [17]:



Although an excess of methyl iodide was used at the methylation stage, the ethyl ester of 1-methyl-2-oxocyclopentanecarboxylic acid was contaminated by the original 2-oxocyclopentanecarboxylic ester, which was removed by agitation of the product with cold caustic potash solution.

Bromination of 2-methylcyclopentanone was carried out in a water-chloroform system at 22-24° in presence of magnesium carbonate (calcium carbonate gave a lower yield). It was found that, when bromination was slow, addition of a few drops of hydrochloric acid was useful. Elimination of hydrogen bromide was effected with the aid of diethylaniline, as in the case of 2-methylcyclohexanone. The yield of 2-methyl-2-cyclopenten-1-one (III) was 50% (on the 2-methylcyclopentanone that reacted).

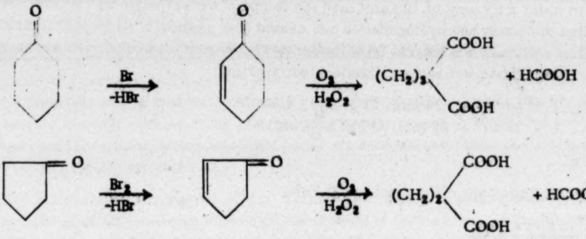
As in the case of 2-methylcyclohexanone, bromination of 2-methylcyclopentanone occurs at the tertiary carbon atom, as the results of the ozonization of the methylcyclopentanone showed. Only succinic and acetic acids were obtained, no methylsuccinic acid being detected:



Bromination of cyclohexanone, unlike that of the two ketones already discussed, proceeds with some difficulty. It was found, however, that it could be carried out smoothly by adding about 20% of cyclohexanol to the cyclohexanone and increasing the amount of bromine correspondingly. The elimination of hydrogen bromide from 2-bromocyclohexanone required a higher temperature (about 150°). The yield of 2-cyclohexen-1-one (IV) was 35% (on the cyclohexanone that reacted).

2-Cyclopenten-1-one (V) was prepared in a precisely similar manner by bromination of cyclopentanone followed by elimination of hydrogen bromide from the 2-bromocyclopentanone formed, but as a result of resinification the yield was only 25% (on the cyclopentanone that reacted).

Ozonization of 2-cyclohexen-1-one and 2-cyclopenten-1-one yielded glutaric and succinic acids respectively:

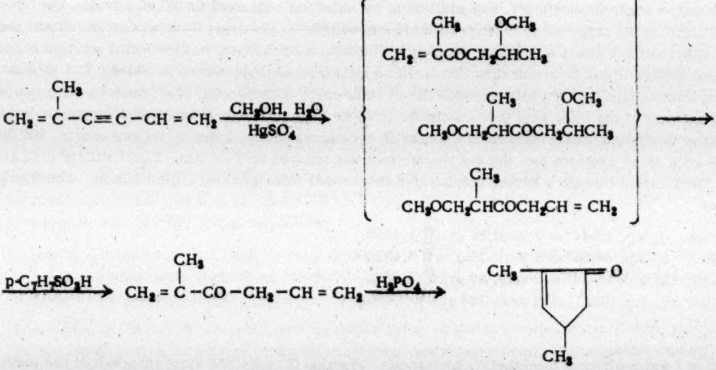

O
Br
-HBr
O
O₃
H₂O₂
(CH₂)₃
COOH
COOH
+ HCOOH
O
Br₂
-HBr
O
O₃
H₂O₂
(CH₂)₂
COOH
COOH
+ HCOOH

Details concerning the α,β-unsaturated cyclic ketones that we have prepared are given in the table.

TABLE

Name of ketone	B.p. (°C/ mm)	n_D^{20}	M.p. of semicarbazone (°C)	
			our results	data in lit.
2-Methyl-2-cyclohexen-1-one	56/ 9	1.4865	206-207 (dec.)	208 [14]
2-Methyl-2-cyclopenten-1-one	52-53/ 15	1.4770	218 (dec.)	220 (dec.) [10]
2-Cyclohexen-1-one	63.5/ 23	1.4872	161	160 [3]
2-Cyclopenten-1-one	45/ 12	1.4720	214-215	214 [12]

We have also simplified the method for the preparation of 2,4-dimethyl-2-cyclopenten-1-one (I). It has been prepared previously from 2-methyl-1,5-hexadien-3-yne in three stages:


CH₂ = C(CH₃) − C≡C − CH = CH₂
CH₃OH, H₂O
HgSO₄
CH₂ = C(CH₃)COCH₂CH(OCH₃)CH₃
CH₃OCH₂CH(CH₃)COCH₂CH(OCH₃)CH₃
CH₃OCH₂CH(CH₃)COCH₂CH = CH₂
p-C₇H₇SO₃H
CH₂ = C(CH₃) − CO − CH₂ − CH = CH₂
H₃PO₄
CH₃
O
CH₃

It was found that the stage in which methanol is eliminated from the methoxy ketones could be omitted, the latter being subjected directly to the treatment with acid (phosphoric or hydrochloric). In this way not only was the overall yield of the dimethylcyclopentanone I increased (by about 40%), but the time required for the preparation was greatly reduced.

EXPERIMENTAL

2-Methylcyclohexanol

A mixture of 500 g of o-cresol (m.p. 190-193°; n_D^{20} 1.545), 20 ml of alcohol, and 15 g of Raney nickel was placed in a two-liter rotating autoclave. Hydrogen at a pressure of 120 atm was introduced from a cylinder, and the autoclave was heated to 120°. After 2 hours 30 minutes the pressure had fallen almost to zero. More hydrogen was passed in under a pressure of 120 atm, and the temperature was raised to 160-170°. After two hours the pressure had fallen to 75 atm and hydrogenation had ceased (the pressure of hydrogen remained constant at a given temperature). The autoclave was rotated for a further two hours at 170°, cooled, and discharged. The contents were filtered, and the filtrate was vacuum-fractionated, yielding:

Fraction I, b.p. 66-78° at 29 mm; 11 g; n_D^{20} 1.4590
Fraction II, b.p. 78-80° at 29 mm; 487 g; n_D^{20} 1.4610

Residue 3 g

Fraction II was 2-methylcyclohexanol; yield 92%.

2-Methylcyclohexanone

A mixture of 350 g of 2-methylcyclohexanol (b.p. 78-80° at 29 mm; n_D^{20} 1.4610) and 250 ml of ether was placed in a three-liter flask fitted with mechanical stirrer, dropping funnel, and thermometer. An oxidizing mixture prepared by dissolving 350 g of sodium dichromate dihydrate and 455 g of sulfuric acid in 1500 ml of water was then added over a period of six hours with vigorous stirring and cooling (a temperature of −3 to −7° was maintained). The reaction mixture was stirred for one hour at −2°, placed in ice overnight, and stirred on the next day for three hours at 0°. The ether layer was separated, and the water layer was extracted four times with ether. The united ether extracts were shaken with potassium carbonate until neutralized, and then dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum-distilled, yielding 296 g (87%) of 2-methylcyclohexanone, b.p. 51-52° at 13 mm; n_D^{19} 1.4482.

2-Methyl-2-cyclohexen-1-one (II)

A mixture of 224 g (2 moles) of 2-methylcyclohexanone, 220 ml of water, and 112 g of finely ground calcium carbonate was placed in a two-liter flask fitted with mechanical stirrer, dropping funnel, and thermometer. The mixture was vigorously stirred for 30 minutes while irradiated with a 1000-watt lamp,, and, with the temperature at 30°, addition of a solution of 320 g (2 moles) of bromine in 260 ml of chloroform was begun.

Bromination began immediately, and addition of bromine was continued for 30-40 minutes, the temperature being maintained in the range 30-35°. When reaction was complete, the upper layer was separated and the water layer was extracted three times with ether. The ether-chloroform extract was washed with a solution of sodium bicarbonate and sodium thiosulfate, and then 320 ml (2.15 moles) of diethylaniline was added. The solution was dried with sodium sulfate, and the solvents were slowly removed at a moderately low pressure over a period of 5-6 hours. The contents of the flask were then heated for three hours in a boiling water bath, the pressure being gradually lowered to 20-25 mm, and a mixture of 2-methyl-2-cyclohexen-1-one, 2-methylcyclohexanone, and diethylaniline gradually came over; toward the end the pressure was reduced to 7-10 mm. The distillate (173 g; n_D^{20} 1.4840) was fractionated through a Fenske column (5-6 theoretical plates) having a glass filling. The fractions obtained were:

Fraction I, b.p. 43-44° at 8 mm; 20 g; n_D^{20} 1.4550
Fraction II, b.p. 44-54° at 9 mm; 19 g; n_D^{20} 1.4720
Fraction III, b.p. 54-56° at 9 mm; 10 g; n_D^{20} 1.4835
Fraction IV, b.p. 56° at 9 mm; 108 g; n_D^{20} 1.4865

Residue 14 g

Fraction I was unchanged 2-methylcyclohexanone. Fraction III contained more than 90% of the methylcyclohexenone II. Fraction IV was pure 2-methyl-2-cyclohexen-1-one (II), b.p. 56° at 9 mm; n_D^{20} 1.4865; d_4^{20} 0.9667. The overall yield was 58% (on the amount of methylcyclohexanone that reacted). In this way we prepared more than 3 kg of 2-methyl-2-cyclohexen-1-one. The semicarbazone melted at 206-207°.

Ozonization of 2-Methyl-2-cyclohexen-1-one (II)

Ozonized oxygen (5% ozone) was passed at 0° for ten hours at 6-7 liters per hour through a solution of 6.8 g of the substance II in 35 ml of chloroform. Water (50 ml) and 30% hydrogen peroxide (5 ml) were added to the ozonide solution, which was then stirred at 50° for three hours. The mixture was cooled and neutralized with sodium carbonate, and the aqueous solution was separated and evaporated to dryness under reduced pressure. The dry salts were dissolved in 18 ml of 30% hydrochloric acid, and the organic acids were extracted by several treatments with ether. The ether solution was dried with magnesium sulfate, and, after removal of ether, volatile acids were distilled off at moderately low pressure. The product was 2.35 g of acetic acid, which was identified by the cacodyl test, absence of formic acid being proved by the calomel method. The residue after removal of volatile acids was vacuum-distilled, and yielded 4.8 g of glutaric acid, b.p. 165°/ 4 mm, which completely solidified (m.p. 96°). In admixture with authentic glutaric acid there was no melting point depression.

Bromination of 2-Methylcyclohexanone with Dioxane Dibromide

Dioxane dibromide was prepared by Favorsky's method [18]. Dry dioxane (b.p. 100-101°; 53 g, i.e., 0.6 mole) was placed in a porcelain beaker and was constantly stirred with a glass rod while bromine (80 g, i.e., 0.5 mole) was added gradually in small portions. The reaction mixture was heated to 60-70° and then cooled, when it solidified to an orange crystalline mass, which was dried in the air between two sheets of filter paper. A theoretical yield (125 g) of dioxane dibromide was obtained.

A mixture of 100 ml of absolute ether and 56 g (0.5 mole) of 2-methylcyclohexanone was placed in an Erlenmeyer flask and was stirred for two hours while dioxane dibromide (125 g, i.e., 0.5 mole) was added in small portions, the temperature being maintained at not above 22-23°. There was a vigorous evolution of hydrogen bromide. When the addition was complete, the reaction mixture was washed with 10% caustic soda solution until neutral, and then with a saturated solution of sodium thiosulfate. The ether layer was separated and mixed with 75 g (0.5 mole) of diethylaniline. Elimination of hydrogen bromide and isolation of the ketone II were performed by the method described in the preceding experiment. The products were 3 g of unchanged methylcyclohexanone and 24.5 g of 2-methyl-2-cyclohexen-1-one, b.p. 61-63° at 14 mm; n_D^{20} 1.4845; the yield was 47% (on the amount of methylcyclohexanone that reacted). When the bromination was performed under the same conditions, but with an addition of calcium carbonate, practically the same results were obtained.

Methylation of Cyclopentanone

Sodamide was prepared by Nieuwland's method [19]. Liquid ammonia (250 ml), sodium (1.5 g), and ferric nitrate (0.15 g) were placed in a three-necked one-liter flask fitted with mercury-sealed stirrer, thermometer, dropping funnel, and tube for passage of air. The flask was cooled with dry ice, and dry air was passed through the mixture until a colorless solution was obtained. More sodium (10 g) was then added, and the mixture was stirred until the blue color disappeared. Absolute ether (200 ml) was added, the cooling mixture was removed, and the ammonia was allowed to evaporate at room temperature. When the temperature in the flask had become equal to that of the room, the mixture was again cooled to −70° and was stirred vigorously while 42 g (0.5 mole) of cyclopentanone was added over a period of five minutes; the temperature rose to −50°. Then, over a period of seven minutes, 85 g (0.59 mole) of methyl iodide was added, and the temperature rose to 15°, in spite of the applied cooling with dry ice. The mixture was stirred for a further ten minutes and then decomposed by addition of 40 g of dry ammonium chloride, which was followed by 250 ml of water. The usual treatment and vacuum distillation yielded 20 g of distillate, b.p. 30-40°/ 15 mm, and 11 g, b.p. 125-129°/ 9 mm.

Fractionation of the first portion of the distillate under ordinary pressure gave the following fractions:

Fraction I, b.p. 80-132°; 1 g; n_D^{20} 1.4390
Fraction II, b.p. 132-136°; 12 g; n_D^{20} 1.4360
Fraction III, b.p. 136-139°; 6 g; n_D^{20} 1.4360

The semicarbazone obtained from Fraction II melted at 175-184°, thus indicating that the fraction was a mixture of various methylation products of cyclopentanone (m.p. of semicarbazones: methylcyclopentanone 170-171°, dimethylcyclopentanone 191° [20]).

Methylation of the sodium derivatives of cyclopentanone in liquid ammonia with methyl iodide and dimethyl sulfate again gave a mixture of products, including, moreover, a considerably greater proportion of high-boiling condensation products.

Oxidation of 2-Methylcyclohexanol

Nitric acid of sp.gr. 1.4 (245 ml) was placed in a three-necked one-liter flask fitted with mechanical stirrer, thermometer, dropping funnel, and reflux condenser. The acid was heated to 108°, and additions were made of 0.25 g of ammonium vanadate and a few drops of 2-methylcyclohexanol; oxides of nitrogen were evolved. The reaction mixture was cooled to 60°, and 50 g of 2-methylcyclohexanol was added at 60-70° over a period of one hour. The mixture was then heated in a water bath for one hour, and was placed in an ice bath overnight.

On the next day the precipitated crystals (9 g) were filtered off under suction; they melted at 108 - 115° and consisted mainly of adipic acid.

The filtrate was evaporated to dryness, and the viscous oil that remained solidified (m.p. 54 - 73°). It was dissolved in 200 ml of ether and set aside at 0° overnight. A further 3 g of adipic acid, m.p. 120 - 128° was precipitated. The greater part of the ether was removed under reduced pressure, and 50 g of crystals, m.p. 60 - 67°, was precipitated; they consisted essentially of 2-methylhexanedioic acid (published values for the melting point of 2-methylhexanedioic acid range from 57° to 64° [21]).

Cyclization of 2-Methylhexanedioic Acid

A mixture of 42 g of 2 methylhexanedioic acid, prepared as above, and 2.1 g of barium hydroxide was placed in a Wurtz flask, which was then heated on a Babo funnel. Distillation began at 285 - 295°, and was continued for two hours. The ketone was salted out of the distillate with potassium carbonate, and was extracted with several portions of ether. The usual treatment and fractionation yielded:

Fraction I, b.p. 125 - 135°; 0.5 g; n_D^{20} 1.4362.
Fraction II, b.p. 135 - 136°; 3.0 g; n_D^{20} 1.4365.
Residue 0.5 g.

The yield was, therefore, 12%.

The semicarbazone prepared from Fraction II melted at 170 - 171°, and the melting point was not depressed by addition of the semicarbazone of 2 methylcyclopentanone. Cyclization by Blanc's method [22], by the use of acetic anhydride, gave 10% of ketone.

Preparation of Diethyl Adipate

A mixture of 1000 ml of benzene, 600 ml of alcohol, 400 g of adipic acid, and 100 ml of concentrated sulfuric acid was placed in a three liter flask fitted with mechanical stirrer and reflux condenser. The mixture was boiled and stirred vigorously for five hours. The benzene layer was separated, and the aqueous layer was extracted twice with benzene. The mixture of water, alcohol, and benzene was distilled off under a moderately low pressure. Distillation of the residue yielded 539 g (97%) of diethyl adipate, b.p. 127 - 128°/13 mm, n_D^{21} 1.4280.

Preparation of the Ethyl Ester of 2-Oxocyclopentanecarboxylic Acid

A mixture of 49.5 g (2.15 moles) of "molecular" sodium (all the sodium must be in a finely dispersed condition) in 1260 ml of absolute toluene, 303 g (1.5 moles) of diethyl adipate, and 15 ml of absolute alcohol was vigorously stirred while being heated under reflux in a water bath in a three necked three-liter flask. The sodium derivatives began to come down at 60 - 70°. The mixture was heated for four hours in the boiling water bath, and the whole mass finally solidified and was set aside overnight. On the next day 200 ml of toluene was added, and the mixture was decomposed with 700 ml of 7% HCl. The toluene layer was separated, and the water layer was extracted with toluene. The united extracts were washed with water and dried with magnesium sulfate. Toluene was removed under reduced pressure, and the residue was distilled, yielding 209 g (89%) of the ethyl ester of 2-oxocyclopentanecarboxylic acid, b.p. 110 - 113°/22 mm, n_D^{21} 1.4525.

Methylation of the Ethyl Ester of 2-Oxocyclopentanecarboxylic Acid

Sodium ethoxide was prepared by dissolving 44.2 g (1.92 g-atoms) of sodium in 1000 ml of absolute alcohol contained in a three-necked three-liter flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. The ethoxide solution was cooled to − 13° and was stirred while 300 g (1.92 moles) of the ethyl ester of 2-oxocyclopentanecarboxylic acid, cooled to − 13° to − 15°, was added over a period of 30 minutes. While stirring was being continued at the same temperature, 275 g (1.97 moles) of methyl iodide was added in one lot, and stirring was further continued while the temperature was raised to that of the room, which took 5 - 6 hours: during this time the voluminous precipitate of sodium derivative gradually disappeared. The reaction mixture was set aside at room temperature overnight, and on the next day the greater part of the alcohol was distilled off under reduced pressure. The residue was treated with 200 ml of water and carefully extracted with ether. The extract was dried with sodium sulfate, the ether was removed, and the residue gave 286 g of distillate, b.p. 106 - 118°/16 mm, n_D^{20} 1.4465. The distillate gave an intense violet color with alcoholic ferric chloride.

Purification of the product from unchanged 2-oxocyclopentanecarboxylic ester was effected by introducing it into a two-liter flask fitted with mechanical stirrer, adding 80 ml of ether, cooling to 0°, and adding rapidly with vigorous stirring a solution, also cooled to 0°, of 32 g of caustic potash in 800 ml of water. Stirring was continued for three minutes. The ether layer was separated, and the water layer was extracted with ether. The ether extracts were dried with calcium chloride, and the solvent was distilled off. Fractionation of the residue yielded 224 g (67%) of the ethyl ester of 1-methyl-2-oxocyclopentanecarboxylic acid, b.p. 116-119°/25 mm, n_D^{20} 1.4465. The product gave no color with ferric chloride.

Preparation of 2-Methylcyclopentanone

A mixture of 510 ml of concentrated hydrochloric acid, 1020 ml of water, and 255 g of the ethyl ester of 1-methyl-2-oxocyclopentanecarboxylic acid was placed in a three-necked three-liter flask fitted with mercury-sealed stirrer and reflux condenser; the latter was fitted with a delivery tube that passed to a flask containing ether for the absorption of methylcyclopentanone vapor carried away by carbon dioxide evolved. The stirred mixture was heated in a water bath for nine hours. During the first two hours there was vigorous evolution of carbon dioxide, which then subsided The solution was cooled and carefully extracted with ether (ten times). The ether extracts (together with the ether from the absorption vessel) were washed with a concentrated solution of sodium carbonate, and then dried with calcium chloride. The solution was transferred to a flask fitted with a large Vigreux column, and the ether was distilled off and the residue fractionated, 98 g (69%) of a fraction of b.p. 136-137°, n_D^{20} 1.4360, being collected. This was 2-methylcyclopentanone; the semicarbazone melted at 170-171°. Altogether, 700 g of methylcyclopentanone was obtained by this method. When alkaline hydrolysis was used, the yield of methylcyclopentanone fell to 50-54%.

Preparation of 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 98 g (1 mole) of 2-methylcyclopentanone, 50 ml of chloroform, 62 g of magnesium carbonate, and 150 ml of water was placed in a three-necked 500-ml flask fitted with mechanical stirrer, dropping funnel, and thermometer The suspension was stirred at 22-24° for two hours while 152 g (0.95 mole) of bromine was added. In order to initiate the reaction it is useful to add 0.5-1 ml of concentrated hydrochloric acid while the stirrer is stopped; this creates a local concentration of hydrogen ions, which promote reaction. When all of the bromine had been added, the chloroform layer was separated and the water layer was extracted three times with ether. To the combined extracts 160 ml (1.07 moles) of diethylaniline was added, and the solution was dried with sodium sulfate. The solvents were distilled off under a moderately low pressure, and, with the pressure reduced to 25 mm, the residue was heated in a boiling water bath, when a mixture of methylcyclopentanone, 2-methyl-2-cyclopenten-1-one, and diethylaniline passed over to the receiver, which was cooled in a freezing mixture. The distillate (67 g) was fractionated through a Fenske column having a glass filling:

Fraction I b.p. 37-39° at 15 mm; 17 g; n_D^{21} 1.4360
Fraction II b.p. 39-52° at 15 mm; 2 g; n_D^{22} 1.4430
Fraction III b.p. 52-53° at 15 mm; 40 g; n_D^{22} 1.4770
Residue 4 g.

Fraction I was almost pure 2-methylcyclopentanone, and Fraction III was pure 2-methyl-2-cyclopenten-1-one. The yield was therefore 51% (on the amount of methylcyclopentanone that reacted).

The semicarbazone melted at 128° (decomposition; in a sealed capillary), and the oxime at 128° (from alcohol). Dane [10] gives 220° (decomposition) and 128° respectively.

Replacement of magnesium carbonate with calcium carbonate lowered the yield to 40%. Replacement of chloroform with carbon tetrachloride lowered the yield still more.

Ozonization of 2-Methyl-2-cyclopenten-1-one (III)

A solution of 2.0 g of 2-methyl-2-cyclopenten-1-one in 30 ml of chloroform was ozonized at 0°, 18 liters of ozonized oxygen (6% ozone) being passed in the course of 4 hr, 30 min. Water (10 ml) and 30% hydrogen peroxide (6 ml) were added to the chloroform solution of the ozonide. The mixture was heated with stirring at 60° for five hours, and then cooled. Sodium carbonate was added until carbon dioxide was no longer evolved (3.5 g altogether), and the water layer was separated, extracted with ether, and acidified with concentrated hydrochloric acid until it was strongly acid to Congo red (5 ml required). On cooling, the solution yielded crystals of acid, which were filtered off under suction and washed with a small amount of cold water. The product, after drying over phosphoric anhydride, was 1.05 g of succinic acid, m.p. 180-181°. A mixture melting point with authentic material showed no depression. The aqueous solution was extracted with benzene, and evaporation of the benzene under reduced pressure yielded a further 0.2 g of less pure succinic acid, m.p. 163-167°. The mother liquor gave a positive cacodyl reaction.

Preparation of 2-Cyclohexen-1-one (IV)

A mixture of 20 g of cyclohexanol, 80 g of cyclohexanone, and 70 g of calcium carbonate (chalk) was placed in a three-necked 500-ml flask fitted with stirrer, dropping funnel, and thermometer, and was warmed to 35°. To the stirred mixture, 182 g of bromine was added over a period of 4-4.5 hours, the temperature being maintained at 35-37° by regulation of the rate of addition of bromine. It was found that at first stirring must be slow, as otherwise the bromination is held back: in that case reaction may be promoted by stopping the stirrer and adding a few drops of cyclohexanol. The chalk must not be too finely ground, and a great excess must be avoided; otherwise, toward the end a difficultly separable emulsion is formed.

When all of the bromine had been added, stirring was continued for a further 30 minutes. The crude bromocompound was separated, and the water layer was extracted three times with ether. The ether extracts were added to the crude bromo compound, the solution was dried with magnesium sulfate, and the solvent was driven off under reduced pressure. It was found that the crude bromo compound had to be used quickly for the HBr-elimination reaction; otherwise it resinified. Also, it was necessary to take the bromo compound in small portions (20-50 g) for the HBr-elimination reaction; otherwise the reaction went with great difficulty and the yield of cyclohexenone fell.

Crude bromo compound (50 g) and diethylaniline (50 g) were placed in a Claisen flask having a Vigreux column. The elimination of hydrogen bromide was effected by rapid heating of the mixture at a residual pressure of 100 mm to 150-155°, 20 g of distillate being obtained. When all of the bromo compound had been treated in this way, the distillates were united and fractionated through a Fenske column having a glass filling; they yielded 20 g of unchanged cyclohexanone and 26 g (35% on the amount of cyclohexanone that reacted) of 2-cyclohexen-1-one, b.p. 63.5° at 23 mm, n_D^{20} 1.4872. The semicarbazone melted at 161° (from alcohol).

Preparation of 2-Cyclopenten-1-one (V)

A mixture of 45 g of cyclopentanone, 5 g of cyclopentanol, 100 ml of water, and 30 g of ground calcium carbonate (chalk) was placed in a three-necked 500-ml flask fitted with mechanical stirrer, dropping funnel, and thermometer. The mixture was warmed to 35°, and 80 g of bromine was added with stirring over a period of three hours. Treatment of the reaction mixture and the elimination of hydrogen bromide were carried out exactly as in the case of cyclohexanone. The yield of 2-cyclopenten-1-one, b.p. 45° at 12 mm, and n_D^{20} 1.4720 was 28%. The melting point of the semicarbazone was 214-215° (from alcohol).

Ozonization of 2-Cyclohexen-1-one (IV)

Ozonization was carried out as in the case of 2-methyl-2-cyclohexen-1-one, and 2.5 g of ketone yielded 1.7 g of glutaric acid, m.p. 97°. A mixture melting point with an authentic sample showed no depression.

Ozonization of 2-Cyclopenten-1-one (V)

Ozonization was carried out as in the case of 1-methyl-2-cyclopenten-1-one, and 4 g of ketone yielded 4.5 g of succinic acid, which melted after two crystallizations at 182-183°. A mixture melting point with an authentic sample showed no depression.

Preparation of 2,4-Dimethyl-2-cyclopenten-1-one (I)

I. Hydration of 2-Methyl-1,5-hexadien-3-yne. Water (180 ml) was placed in a five liter flask fitted with an efficient mechanical stirrer, and 11 g of sulfuric acid and 15 g of mercuric sulfate were dissolved successively in the water. Stirring was begun, and a solution of 800 g of 2-methyl-1,5-hexadien-3-yne in 1800 ml of methanol was added. The mixture was heated to 60°, and stirring was continued at that temperature for six hours, 1 g of finely ground mercuric sulfate being added after each hour. The mixture was set aside over night, and on the next day stirring was renewed and the temperature was brought to 60°; stirring continued for a further six hours, and 7 g of mercuric sulfate was added at the beginning and then 1 g per hour for the remaining time.

The liquid was transferred to a flask having a Vigreux column, and the bulk of the methanol was removed in a water bath at not above 35° under somewhat reduced pressure. The residue was neutralized to litmus with a solution of sodium methoxide (10 g of sodium in 200 ml of methanol), and 500 ml of ether and 50 g of zinc dust were added. The mixture was shaken vigorously and then allowed to stand for 4-5 hours with periodic shaking. The solution was filtered, 5-6 ml of dimethylaniline was added, and ether was removed in a water bath. Residual ether, methanol, and water were then removed under a moderately low pressure, and the residue was vacuum-distilled from a Claisen flask. Distillation was continued until, at a bath temperature of 130°, practically nothing further came over. The yield of methoxy ketone mixture, b.p. 70-100° at 20 mm was 900-960 g.

II. Cyclization of the Mixture of Methoxy Ketones with the Aid of Phosphoric Acid. The above described mixture of methoxy ketones (580 g) was placed in a three necked, two liter flask fitted with sealed mechanical stirrer, thermometer, and dropping funnel, and was stirred while 580 ml of phosphoric acid of sp.gr. 1.77 was added. The temperature gradually rose and attained 60-65° when about half of the acid had been added. Cooling was applied so that the temperature did not exceed 70°. Addition of acid occupied about one hour, and the reaction mixture was then heated at 70° for a further two hours. It was then cooled, 500 ml of water was added, and the mixture was stirred and cooled with water while 400 g of anhydrous sodium carbonate was added in small portions. The upper layer was separated, and the lower layer was extracted three times with ether (500 ml altogether). The combined extracts were neutralized with potassium carbonate powder (about 50 g), and then filtered. The ether was driven off, and the residue was distilled from a flask having a Vigreux column. Two fractionations yielded 300-325 g (49-53% on the amount of methylhexadienyne taken) of 2,4-dimethyl-2-cyclopenten-1-one, b.p. 61-62° at 16 mm, n_D^{20} 1.4675-1.4685.

III. Cyclization of the Mixture of Methoxy Ketones with the Aid of Hydrochloric Acid. A mixture of 1080 g of the above described mixture of methoxy ketones (b.p. 70-100° at 20 mm) and 2160 g of 18% hydrochloric acid was stirred for four hours at 80-85° in a three necked, five liter flask provided with sealed mechanical stirrer, thermometer, and dropping funnel. The mixture was then cooled and neutralized with sodium carbonate (about 550 g). The upper layer was separated, and the lower layer was extracted three times with ether (about 1000 ml altogether. The combined extracts were dried with calcined potassium carbonate and filtered. Ether was distilled off through a column, and the residue was fractionated from a flask having a good Vigreux column.

Two fractionations gave 600-630 g (55-59% on the amount of methylhexadienyne taken) of 2,4-dimethyl-2-cyclopenten-1-one, b.p. 50-52° at 9 mm, n_D^{20} 1.4670. The head and tail fractions amounted to 60 g; there was 215-220 g of undistilled residue.

SUMMARY

1. A general method has been developed for the preparation of α,β-unsaturated cyclic ketones. There are two stages: bromination of a cyclic ketone in presence of calcium or magnesium carbonate; and elimination of hydrogen bromide from the bromo ketone formed, which is effected by heating it in presence of diethylaniline.

2. 2-Methyl-2-cyclohexen-1-one (58% yield), 2-methyl-2-cyclopenten-1-one (50% yield), 2-cyclohexen-1-one (35% yield), and 2-cyclopenten-1-one (25% yield) have been prepared by this method.

3. It has been proved that, in the bromination of 2-methylcyclohexanone and of 2-methylcyclopentanone, bromine attacks the tertiary carbon atom, and not a secondary carbon, as asserted previously by some workers.

4. The method of preparing 2,4-dimethyl-2-cyclopenten-1-one has been simplified and improved.

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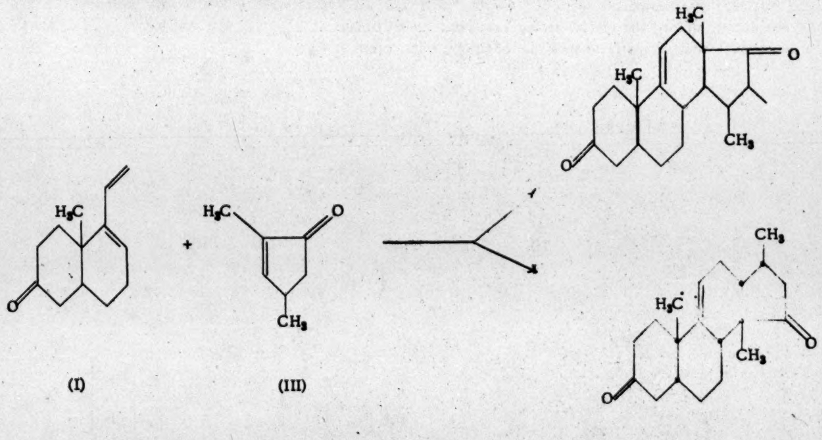
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVIII. CONDENSATION OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE WITH 2,4-DIMETHYL-2-CYCLOPENTEN-1-ONE*

I. N. Nazarov and I. V. Torgov

The simple method that we have developed in our laboratory for the preparation of polycyclic compounds having angular methyl groups [1] has made it possible, for the first time, to carry out the total synthesis of steroid ketones belonging to the cis-cis series. An important intermediate product for the synthesis of these compounds is the vinyl-2(1H)-naphthalenone (I), which has been described in detail in a previous communication [2]. By condensation of this substance with 2,4-dimethyl-2-cyclopenten-1-one (III), we have already prepared an isomer of methylandrostenedione [1], although the structure of this has not been established.

In the present work we have made a detailed study of the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-dimethyl-2-cyclopenten-1-one (III). In this condensation, depending on the orientation of the reacting compounds, two series of isomers may be formed: one in which the keto group is in the 17-position (the "normal" structure), and one in which it is in the 15-position (the "inverted" structure):



(I) (III)

The number of isomers in each series is determined by the number of asymmetric carbon atoms (marked by large dots) and by the cis-addition rule that applies in the diene condensation. It will be readily seen that there is a possibility of obtaining eight racemates in each structural series. For "inverted" structures of the cis-cis series, for example, all of the eight possible racemates are represented below:

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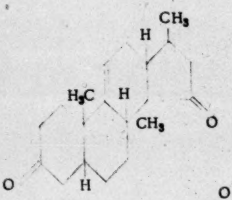
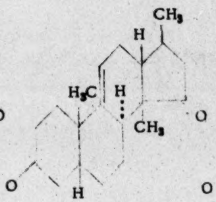
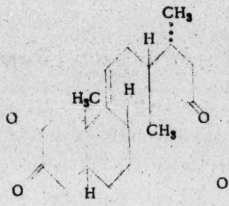
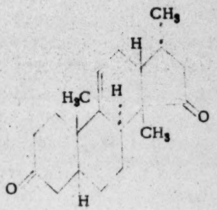
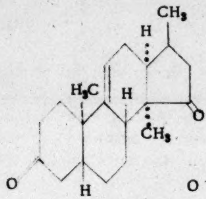
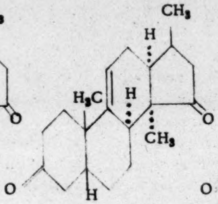
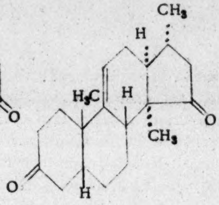
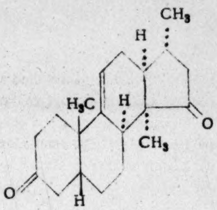
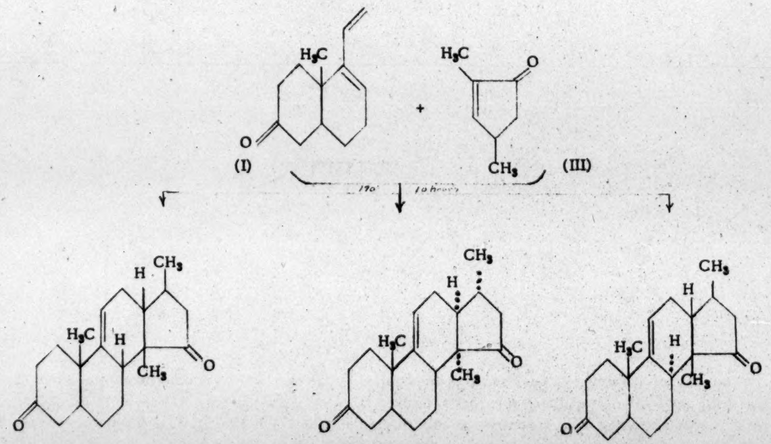









Actually, when the diene (I) was heated with 5-8 times its weight of the dimethylcyclopentenone (III) (170°, 10-13 hours), a 55% yield was obtained of a mixture of isomeric steroid ketones, from which three isomers of 10,14,17-trimethyl-9-cardosterene-3,15-dione (IV A, IV B, and IV C in the proportions of 95:4:1 approximately) were isolated (the nomenclature used here for such synthetic steroids is that proposed by Nazarov [3]). It was found that all three compounds were of "inverted" structure, and the difference between the isomers IV A and IV B was determined by the spatial arrangement of the substituents at $C_{13}-C_{14}$, and that between IV C and IV A lay in the difference in spatial disposition of the hydrogen atom at C_8.



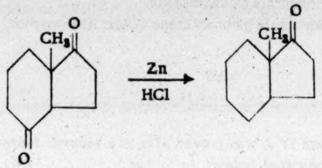
(IV A)
m.p. 166-167°

(IV B)
m.p. 155-156°

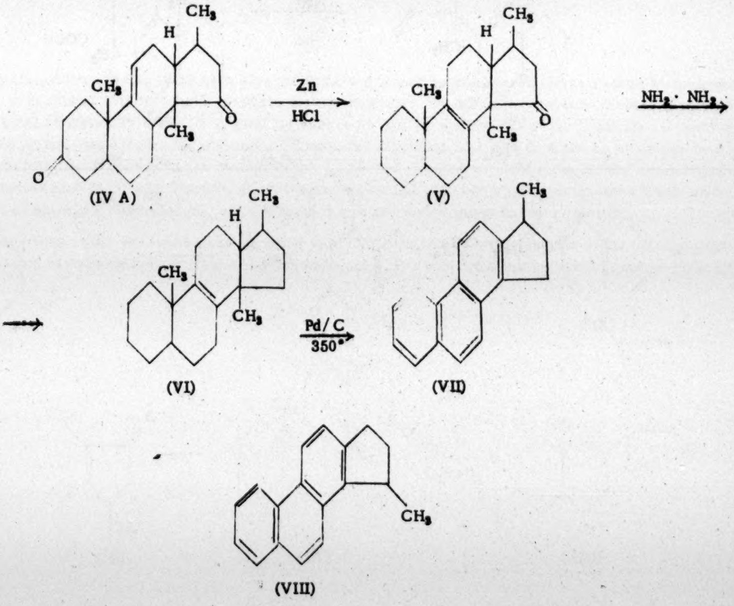
(IV C)
m.p. 203-205°

The choice of a spatial configuration for the diketone IV A from among the eight structures given above was made on the basis of the rules of the diene synthesis; for there are no direct proofs of the relative spatial dispositions of the substituents in this diketone. Stuart models that we made of the molecules showed that all eight structures were quite possible.

In the proof of the structures of the steroid diketones obtained, an important part was played by the difference in activity of the keto groups in rings A and D. Whereas the keto group in ring A readily underwent Clemmensen reduction, the keto group in ring D was not affected by this treatment. The inertness of a keto group in the five-membered ring D has been noted on several occasions in the literature. Isomers of estrone and epiandrosterone, for example, which have carbonyl groups in the 16-position, are not reduced under these conditions [4], and reduction of tetrahydro-7a-methyl-1,4(5H)-indandione results in removal of only the keto group in the six-membered ring [5]:



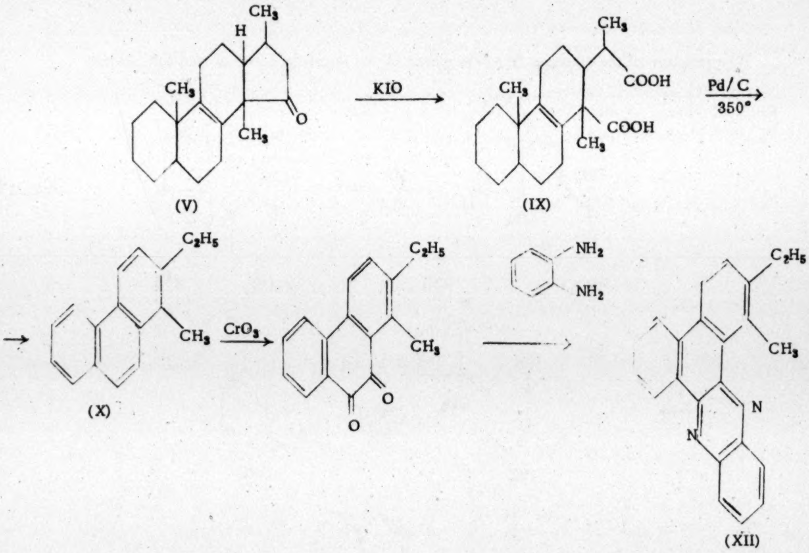
The structure of the diketone IV A was proved by the following series of transformations:



The diketone IV A was converted by Clemmensen reduction into 10,14,17-trimethyl-8-cardosterene-15-one (V), m.p. 104°, which was further converted by the Kizhner reaction into 10,14,17-trimethyl-8-cardosterene (VI). Dehydrogenation of this hydrocarbon in the presence of palladized charcoal followed by chromatographic treatment led to the isolation of the so-called Diels hydrocarbon, 16,17-dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (VII). The melting points of the hydrocarbon and of its compound with trinitrobenzene agreed with the values given in the literature and were greatly different from the corresponding values for 16,17-dihydro-15-methyl-15H-cyclopenta[a]-phenanthrene (VIII), which should have been formed if the original diketone had the "normal" structure.

Substance	Melting point (°C)	
	of hydrocarbon	of trinitrobenzene derivative
16,17-Dihydro-15-methyl-15H-cyclopenta[a]phenanthrene.	76 – 77[6]	143 – 144[6]
16,17-Dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (Diels hydrocarbon)	125 – 126[7]	147[7]
	123 – 124[8]	148[6]
	124 – 125[9]	150[8]
Hydrocarbon obtained	121.5–122	148

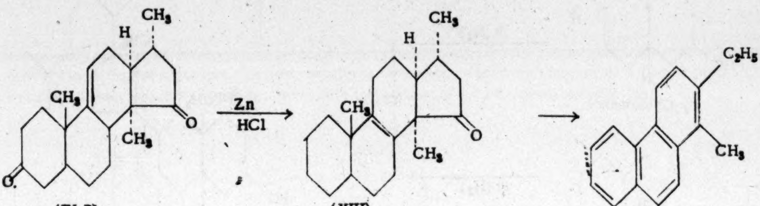
The structure of the diketone IV A was proved also in a second, independent way; namely, by its conversion into phenanthrene derivatives as indicated below:



The monoketone (V) was oxidized with alkaline iodine in methanol solution to the dicarboxylic acid (IX) which on dehydrogenation yielded the known 2-ethyl-1-methylphenanthrene (X). (X) was converted into the quinone (XI), and then into the quinoxaline (XII). The melting points of (X) and (XII) agreed with those given in the literature, and they were quite different from those of 1-ethyl-2-methylphenanthrene and its derivative, which would correspond to the "normal" structure. The melting points of the isomeric quinones are close together and therefore not very characteristic.

Substance	Melting point (°C)		
	of hydrocarbon	of quinone	of quinoxaline
1-Ethyl-2-methylphenanthrene	79 – 80 [10,11]	157 – 159	146 – 147
2-Ethyl-1-methylphenanthrene	100 [10]	163	108
Our 2-ethyl-1-methylphenanthrene	96	155 – 157	108

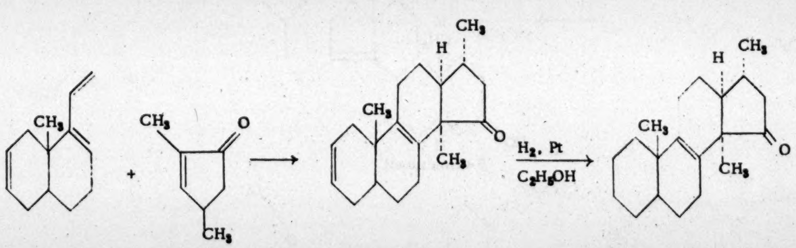
The structure of the diketone IV B was proved by the same method. Clemmensen reduction of IV B yielded the monoketone (XIII), m.p. 122°, which was distinct from the monoketone (V). By the series of transformations already described, it was converted into 2-ethyl-1-methylphenanthrene (X), which was characterized by its melting point and by its conversion into the quinone (XI) and the quinoxaline (XII):



(IV B) (XIII) (X)

As the monoketones (V) and (XIII) both give the same ethylmethylphenanthrene (X) as a result of analogous transformations, it is evident that they have identical carbon skeletons; the difference between them, and therefore between the original diketones IV A and IV B, must lie only in the spatial dispositions of the hydrogen and methyl at $C_{13} - C_{14}$. We do not consider that the difference between the diketones IV A and IV B can be explained by a difference in the spatial arrangement of the methyl in the 17-position because we shall show in later communications that the condensation of (I) with 2-methyl-2-cyclohexen-1-one and with 2-methyl-2-cyclopenten-1-one leads to the formation of analogous stereoisomers, and yet there is now no methyl group in the 17-position.

The monoketone (XIII) was found to be identical with that obtained by hydrogenation of the condensation product of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (XIV) with 2,4-dimethyl-2-cyclopenten-1-one (III)*:



(XIV) (III) (XV) (XIII)

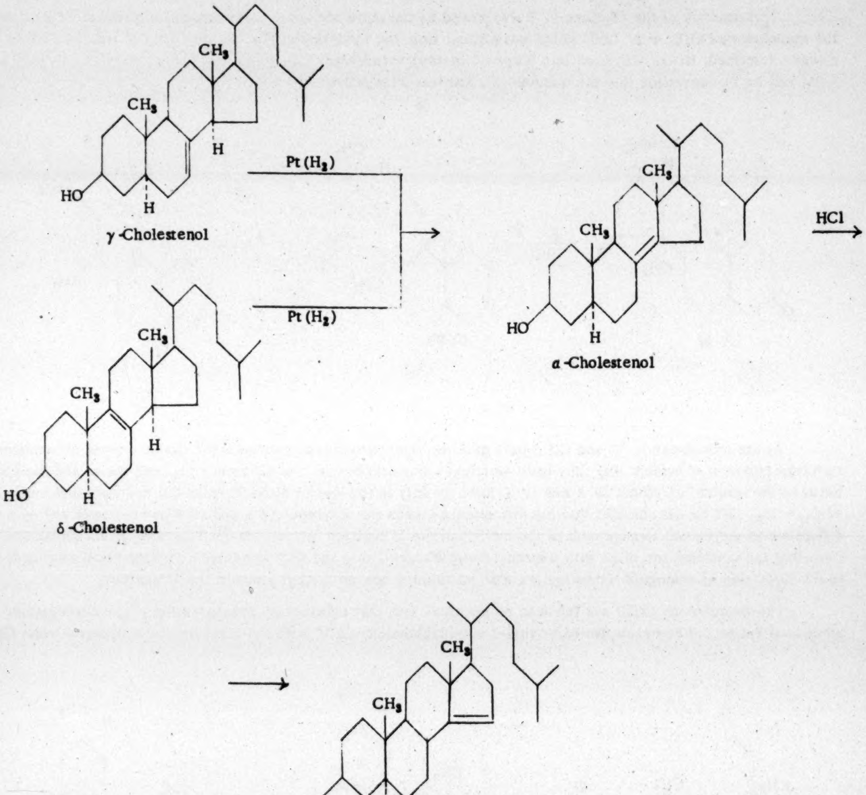
---

* This condensation is described in the next paper in this journal.

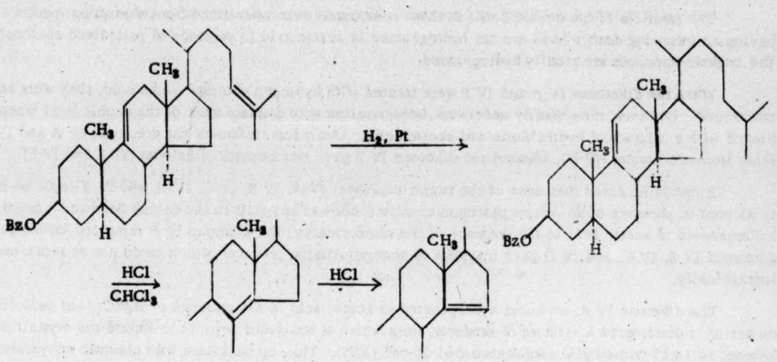
Clemmensen reduction of the isomer IV C gave the same monoketone (V) as that obtained by reduction of the diketone IV A. It is most probable that the difference between the diketones IV A and IV C lies in the spatial disposition of the hydrogen at C_8. Under the conditions of Clemmensen reduction, the double bond is displaced from 9(11) to 8(9) in both isomers, and the same monoketone (V) is therefore obtained.

Displacement of a double bond in the presence of acids and catalysts occurs very readily in polycyclic systems.

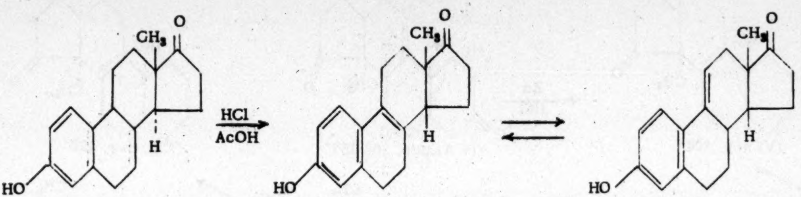
Thus the following transformations have been effected in the cholestane series [12]:


CH₃
CH₃
H
HO
H
γ-Cholestenol
Pt (H₂)
Pt (H₂)
CH₃
CH₃
H
HO
H
δ-Cholestenol
CH₃
CH₃
HO
H
α-Cholestenol
HCl
CH₃
CH₃
HO
H
β-Cholestenol

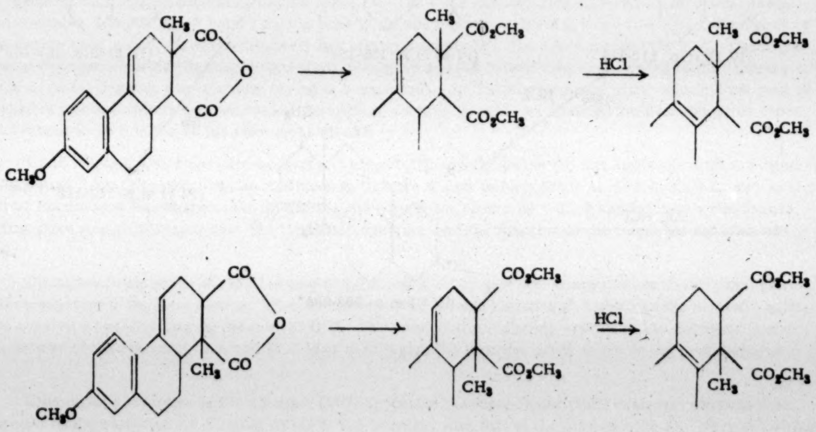
Similar transformations have been effected also for related compounds: ergostenols [13], spinasterols [14], and zymosterol [15]. The case of zymosterol is of particular interest because the analogy with our diketones is here the closest (with respect to the position of the double bond):


CH$_3$
CH$_3$
H
BzO
H
H$_2$, Pt
CH$_3$
CH$_3$
H
BzO
H
HCl
CHCl$_3$
CH$_3$
HCl
CH$_3$

Under the action of hydrogen chloride, equilin is converted, with displacement of a double bond, into 8(9)-dehydroisoestrone, which will undergo reversible isomerization into 9-dehydroestrone [16].


O
CH$_3$
H
HO
HCl
AcOH
O
CH$_3$
H
HO
O
CH$_3$
H
HO

When citraconic anhydride is condensed with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, acids are formed in in which, as Miescher has shown, the double bond is readily displaced to the inter-ring position in presence of hydrogen chloride [17]:

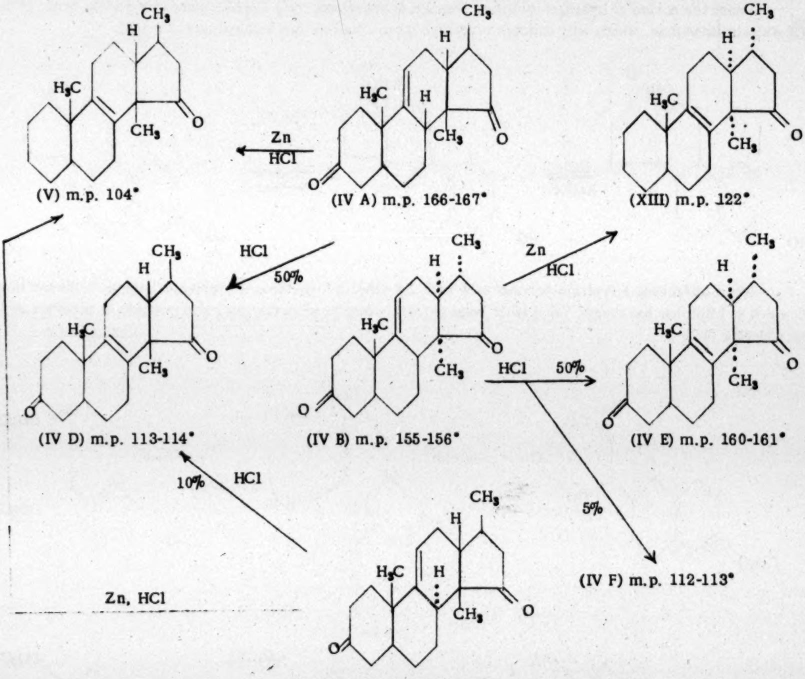

CH$_3$
CO
O
CO
CH$_3$O
CH$_3$
CO$_2$CH$_3$
CO$_2$CH$_3$
HCl
CH$_3$
CO$_2$CH$_3$
CO$_2$CH$_3$
CO
O
CH$_3$
CO
CH$_3$O
CO$_2$CH$_3$
CO$_2$CH$_3$
CH$_3$
HCl
CO$_2$CH$_3$
CO$_2$CH$_3$
CH$_3$

The positions of the double bonds in these compounds were established from absorption spectra. Compounds having an inter-ring double bond are not hydrogenated in acetic acid in presence of palladized charcoal, whereas the original compounds are readily hydrogenated.

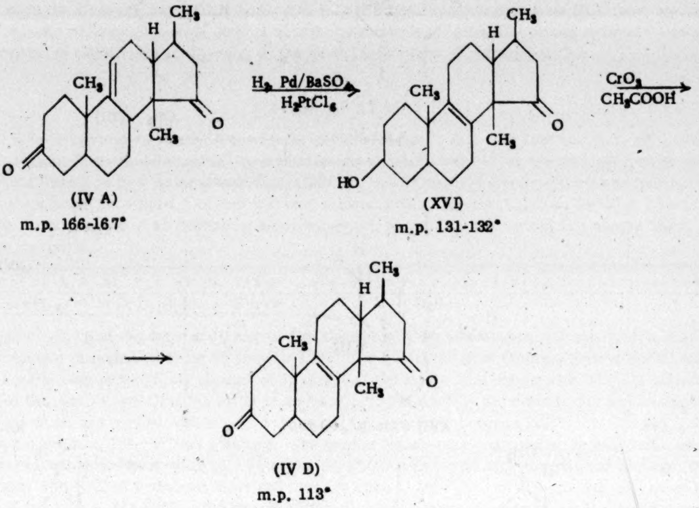
When the diketones IV A and IV B were treated with hydrogen chloride in the cold, they were recovered unchanged. However, they readily underwent isomerization with displacement of the double bond when they were heated with a mixture of hydrochloric and acetic acids. Under this treatment the diketones IV A and IV C gave the same isomeric ketone (IV D), whereas the diketone IV B gave two isomeric diketones (IV E and IV F).

It should be noted that none of the isomeric ketones IV A, IV B, IV C, IV D, and IV E could be hydrogenated in alcohol in presence of an Adams platinum catalyst; nor was any shift in the double bond to be noted. When hydrogenated in acetic acid in the presence of the same catalyst, the diketone IV A remained unchanged, and the diketones IV B, IV C, and IV D gave mixtures of noncrystallizing products, which could not be separated chromatographically.

The diketone IV A, on being hydrogenated in acetic acid in the presence of H_2PtCl_6 and palladium carried on barium sulfate, gave a mixture of products, from which it was found possible to isolate the crystalline hydroxy ketone, 10,14,17-trimethyl-8-cardosteren-3-ol-15-one (XVI). This, on oxidation with chromic anhydride, yielded



10,14,17-trimethyl-8-cardosteren-3,15-dione (IV D). Under comparatively severe conditions of hydrogenation, therefore, the double bond of the diketone IV A was preserved, being merely displaced from the 9(11)- to the 8(9)-position:



(IV A)
m.p. 166-167°

(XVI)
m.p. 131-132°

(IV D)
m.p. 113°

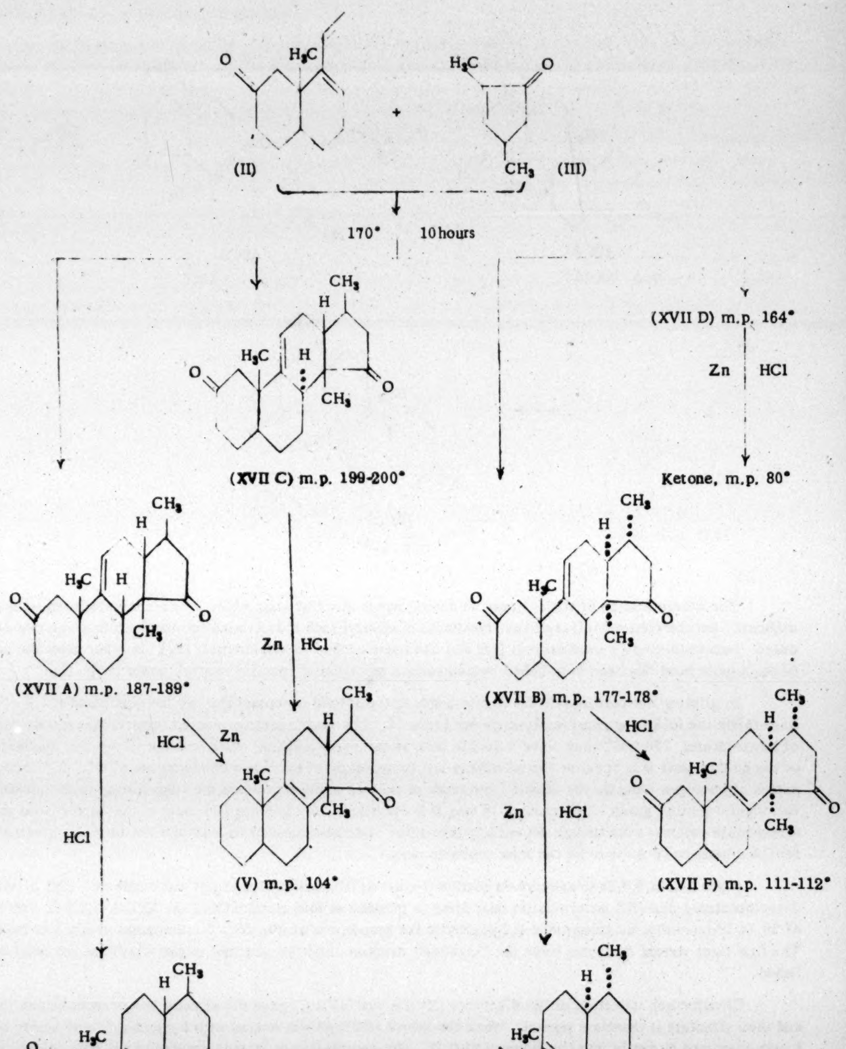
The determination of the positions of double bonds in tetracyclic systems by a chemical method is extremely difficult. For the cholestenols (and the ergostenols similarly) such a determination has been made in two cases only: 7-cholesten-3-ol(γ-cholestenol) [18] and 14-cholesten-3-ol (β-cholestenol) [19]. In other cases the position of the double bond has been established by comparison of values of specific rotatory power [20].

In alloting the positions of the double bonds in the steroid diketones that we have prepared (IV A – E), we have taken the following considerations as our basis: 1. The main reaction product formed over a wide range of temperatures, 130-200°, must have a double bond in the 9(11)-position, since it is not likely that displacement of the double bond will occur at the relatively low temperature of the diene condensation (130°). 2. Under the action of hydrogen chloride the double bond tends to take up a place between the rings (owing to the presence of the angular methyl group, displacement in ring D is excluded). 3. The displacement of the double bond may be a reversible process, even though not readily reversible. On these grounds we consider the formulas given above for the diketones IV A – E to be the most probable ones.

When 3,4,4a,5,6,8a-hexahydro-8a-methyl-7-vinyl-2(1H)-naphthalenone (II) was condensed with 2,4-dimethyl-2-cyclopenten-1-one (III) under similar conditions, a mixture of four isomers (XVII A, XVII B, XVII C, and XVII D) of 10,14,17-trimethyl-9-cardosterene-2,15-dione in the proportions of 60 : 35 : 3 : 2 approximately was formed. The first three steroid diketones have the "inverted" structure, and the structure of the fourth has not been established.

Clemmensen reduction of the diketones (XVII A and XVII C) gave the already known monoketone (V), and their structure is therefore proved. When the isomer (XVII A) was heated with hydrochloric and acetic acids, it was converted partially into the isomer (XVII E). The considerations already applied to the determination of the structures of the diketones IV A and IV C lead us to regard the formulas given above as the most probable ones.

Clemmensen reduction of the diketone (XVII B) yielded the monoketone (XIII) described above so that the spatial configuration of the diketone (XVII B) was identical with that of the diketone (IV B). When the diketone (XVII B) was heated with hydrochloric and acetic acids, isomerization occurred only to a very slight extent, which is in contrast with the behavior of the diketone (IV B), which underwent 50% isomerization. Nevertheless, it was found possible to obtain a 5% yield of the isomeric diketone (XVII F).


(II)
(III)
170°
10 hours
(XVII C) m.p. 199-200°
(XVII D) m.p. 164°
Zn HCl
Ketone, m.p. 80°
(XVII A) m.p. 187-189°
Zn HCl
(XVII B) m.p. 177-178°
HCl Zn
HCl
(V) m.p. 104°
(XVII F) m.p. 111-112°
HCl
Zn HCl
(XVII E) m.p. 139-140°
(XIII) m.p. 122°

Clemmensen reduction of the isomer (XVII D) yielded a monoketone of m.p. 80°, which was different from the monoketones (V) and (XIII). The amount of the original diketone available was too small to permit further investigation; the most that can be said is that it has a different structure from that of the other isomers. The diketones (XVII A), (XVII B), and (XVII C) do not undergo hydrogenation in the presence of an Adams platinum catalyst, neither in alcohol nor in acetic acid.

Hence, when the dienes (I) and (II) are condensed with the dimethylcyclopentanone (III), there are formed in every case a mixture of isomeric steroid ketones of inverted structure, which differ among themselves only in the spatial disposition of substituents at $C_{13}-C_{14}$ or the spatial disposition of hydrogen at C_8.

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm, n_D^{20} 1.5270) were prepared by the method described in a previous communication [2]. 2,4-Dimethyl-2-cyclopenten-1-one (III) was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one, as described previously [21] (b.p. 58-59° at 15 mm; n_D^{20} 1.4675). The melting points of all substances described in this paper were determined in a copper block; all temperatures are corrected.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2,4-Dimethyl-2-cyclopenten-1-one (III)

A mixture of 12.3 g of the dienone (I) and 96 g of the dimethylcyclopentenone (III) was heated in an atmosphere of carbon dioxide in sealed tubes for 13 hours at 170°. The excess (88 g) of the dimethylcyclopentenone was distilled off in a water bath at a residual pressure of 15 mm, and the residue was mixed with 20 ml of petroleum ether and 1 ml of benzene. Crystallization set in immediately. After one day the crystals that had separated were filtered off under suction and washed with a mixture of petroleum ether and benzene (10:1). In this way 7.9 g of a mixture of isomers of m.p. 130-140° was obtained. The mother liquor was evaporated down under reduced pressure, and residual dimethylcyclopentenone (2.0 g) was removed in a water bath at 1 mm residual pressure. The residue was diluted with 5 ml of petroleum ether and then set aside at 8-10° for two days. A second crop of crystals separated (0.15 g; m.p. 150-200°). The second mother liquor was evaporated down, and excess of dienone (2.7 g; n_D^{20} 1.5235) was distilled off at 1 mm and at a bath temperature of not above 150°; the residue was dissolved in a mixture of 3 ml of petroleum ether and 1 ml of benzene. After two days a third crop of crystals was separated (0.3 g; m.p. 140-150°). In this way 8.35 g altogether of a mixture of crystalline isomers of 10,14,17-trimethyl-9-cardosterene-3,15-dione was obtained. The yield was 43% on the amount of the dienone (I) taken, or 55% on the amount of dienone that reacted.

By fractional crystallization of the first and third batches of crystals from a mixture of petroleum ether and benzene (3:1), 6.7 g of isomer (IV A), m.p. 166-167°, and 0.15 g of isomer (IV B), m.p. 156-156.5°, were isolated. Their separation was rendered difficult by the fact that they have almost the same solubility and separate out together. By a combination of slow crystallization with mechanical separation of the required isomers, it was found possible to effect the separation. In other experiments somewhat greater amounts of the isomer (IV B) [with respect to the isomer (IV A) were obtained than those shown above. In one experiment, for example, 0.12 g of isomer (IV B) was obtained together with 1.6 g of isomer (IV A). The isomer (IV A) has been isolated and characterized previously [1]. The isomer (IV B) forms white plates, m.p. 156-156.5°.

Found %: C 79.8; 79.8; H 9.45; 9.6
$C_{20}H_{28}O_2$. Calculated %: C 80.0 H 9.4

A mixture of isomers (IV A) and (IV B) melts at 130-140°.

By crystallization of the second crop of crystals from a mixture of methanol and benzene (3:1), 70 mg of the isomer (IV C), m.p. 203-205°, was isolated in the form of white needles.

Found %: C 80.1; 80.25; H 9.4; 9.5
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Isomerization of the Diketone (IV A)

A mixture of 260 mg of the diketone (IV A), m.p. 166-167°, 5 ml of acetic acid, 5 ml of concentrated hydrochloric acid, and 6 ml of toluene was boiled under reflux for ten hours The toluene layer was separated, and the aqueous layer was diluted with an equal amount of water and extracted with benzene. The combined benzene-toluene extracts were neutralized by agitation with 10% caustic soda. After removal of solvent under reduced pressure, the residue was crystallized from 1 ml of alcohol, yielding 140 mg of the diketone (IV D) in the form of large prisms, m.p. 114-115°.

Found %: C 79.8; 80.2; H 9.6; 9.6
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

When a solution of the diketone (IV A) in acetic acid was treated with hydrogen chloride in the cold for 12 hours, no isomerization occurred, and the substance was recovered unchanged. In a similar way, no isomerization occurred when a xylene solution of the diketone (IV A) was heated at 170° for seven hours.

Isomerization of the Diketone (IV B)

This reaction was carried out similarly to the preceding one. From 285 mg of the diketone (IV B), m.p. 156-156.5°, 130 mg of the diketone (IV E) was obtained in the form of long prisms (from alcohol), m.p. 161-162°.

Found %: C 79.9; 79.8; H 9.4; 9.3
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

The diketone (IV E), when mixed with the original diketone (IV B) or with the diketone (IV A), gave a strongly depressed melting point. From the mother liquor 15 mg of the isomer (IV F) was isolated in the form of needles, m.p. 112-113° (from alcohol).

Found %: C 80.1; 79.8; H 9.5; 9.4
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

A mixture melting point test of (IV F) and (IV D) gave a strong depression. An attempt to isomerize the diketone (IV B) by the action of hydrogen chloride in acetic acid at 20° was not successful; the diketone was returned unchanged.

Isomerization of the Diketone (IV C)

The isomerization was carried out in a similar way on 70 mg of the substance of m.p. 203-205°. The diketone was found to be fairly stable, and part of it (30 mg) was recovered after the experiment in an impure form (m.p. 180-200°). It was found possible to isolate 6 mg of the diketone (IV D), m.p. 115-116°, from the mother liquor. In admixture with the diketone (IV D) obtained above, there was no depression in melting point.

Clemmensen Reduction of the Diketone (IV A)

A mixture of 2 g of the diketone (IV A), m.p. 166-167°, 25 ml of acetic acid, 25 ml of concentrated hydrochloric acid, 20 ml of toluene, and 10 g of amalgamated zinc was boiled for 3 hours, 30 minutes under reflux. More zinc was then added (3.5 g), and the mixture was boiled for a further three hours. The reaction mixture was cooled, the toluene layer was separated, and the water layer was extracted three times with ether. The ether and toluene layers were united, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was driven off, and the residue was diluted with 7-8 ml of ether and set aside in the cold to crystallize, when 1.0 g (52%) of the ketone (V) was obtained in the form of white plates, m.p. 100-102°. The pure ketone melted at 103-104° (from petroleum ether).

Found %: C 83.9; 83.75; H 10.8; 10.6
$C_{20}H_{30}O$. Calculated %: C 83.85; H 10.6

The dinitrophenylhydrazone formed beautiful yellow needles, m.p. 232-233° (from alcohol).

Clemmensen Reduction of the Diketone (IV C)

A mixture of 75 mg of the diketone (IV C), m.p. 203-205°, 5 ml of acetic acid, 10 ml of concentrated hydrochloric acid, 5 ml of toluene, and 1.5 g of amalgamated zinc was boiled for 3 hours, 30 minutes under reflux.

The toluene layer was separated, and the aqueous layer was extracted twice with benzene. The combined extracts were neutralized, and solvent was driven off under reduced pressure. The residue rapidly crystallized out. Crystallization from 0.5 ml of ether at −15° yielded 21 mg of the ketone (V), m.p. 100-101°. A mixture melting point with a sample of the ketone obtained in the preceding experiment was not depressed.

Clemmensen Reduction of the Diketone (IV B)

The reduction was performed as in the preceding experiments. From 400 mg of the diketone (IV B), m.p. 156-156.5°, 50 mg of the ketone (XIII), m.p. 120-122° (from hexane), was obtained.

Found %: C 83.9; H 10.8
$C_{20}H_{30}O$. Calculated %: C 83.85; H 10.6

A mixture melting point with the ketone obtained by hydrogenation of the ketone (XV) and having m.p. 122° was not dpressed. The mother liquor remaining after the separation of the ketone (XIII) crystallized out almost complete. It was used without purification for the oxidation reaction.

Kizhner Reduction of the Ketone (V)

To a solution of 1.7 g of the ketone (V), m.p. 100-102°, in 5 ml of dioxane, 1.2 ml of hydrazine hydrate and 5 ml of diethylene glycol were added, and the mixture was heated for a few minutes in a water bath. It was then transferred to a Favorsky flask having ground joints, a solution of 1.4 g of sodium in 36 ml of diethylene glycol was added, and the almost homogeneous mixture was heated at 205-210° in a feeble current of nitrogen for 15 hours. Several milliliters of distillate came over. The reaction mixture was diluted with 50 ml of water and extracted twice with 50 ml portions of ether. The ether extract was shaken with 10% hydrochloric acid and dried with magnesium sulfate. The ether was driven off, and the residue was vacuum distilled, yielding 1.3 g (81%) of the hydrocarbon (VI) as a colorless liquid, not very viscous and almost odorless, b.p. 130-135° at 1 mm, n_D^{20} 1.5200.

Found %: C 87.9; 88.15; H 11.9; 12.1.
$C_{20}H_{32}$. Calculated %: C 88.2; H 11.8.

Dehydrogenation of the Hydrocarbon (VI)

A mixture of 1.1 g of the hydrocarbon (VI), 0.5 g of palladized charcoal (10% Pd), and 18 ml of dry benzene was heated in a nitrogen atmosphere in a rotating autoclave at 350° for six hours, the initial pressure being 30 atm. The reaction mixture was filtered, benzene was removed under reduced pressure, and the noncrystallizing residue was dissolved in 10 ml of petroleum ether and submitted to chromatography on 10 g of aluminum oxide, when the following fractions were obtained:

Fractions I – III	Each 4 ml of petroleum ether	587 mg	Oil
Fractions IV – VI	Ditto	129 mg	Crystals impregnated in oil, m.p. 80-85°
Fractions VII – VIII	Ditto	42 mg	Crystals, m.p. about 100°
Fractions IX – XI	Each 4 ml of a mixture of petroleum ether and benzene (7:1)	97 mg	Crystals impregnated in oil
Fractions XII – XIII	Each 4 ml of a mixture of petroleum ether and benzene (3:1)	9 mg	Oil
Fraction XIV	Each 4 ml of a mixture of petroleum ether and benzene (1:1)	2 mg	Ditto
Fractions XV – XVI	Each 4 ml of a mixture of petroleum ether and benzene (1:3)	9 mg	Ditto
Fractions XVII – XVIII	Each 4 ml of benzene	6 mg	Ditto
	Total	881 mg	

Crystallization of fractions VII – XI from 1 ml of petroleum ether yielded 25 mg of nodular crystals, m.p. 111-113.5°. A second crystallization from 0.5 ml of petroleum ether yielded 10 mg of the Diels hydrocarbon (VII), m.p. 121.5-122°.

Found %: C 92.85; 92.8; H 7.0; 7.1
$C_{18}H_{16}$. Calculated %: C 93.06; H 6.94

With trinitrobenzene it formed yellow needles, m.p. 148-149° (from methanol).

The mother liquors from the crystallizations were combined with Fractions IV – VI, and the mixture was crystallized from 0.7 ml of petroleum ether. A further 41 mg of the Diels hydrocarbon (VII), m.p. 118-119°, was obtained. Recrystallization of this from petroleum ether yielded 20 mg of pure hydrocarbon (VII), m.p. 120.5-121°.

Oxidation of the Ketone (V) to the Dicarboxylic Acid (IX)

To a stirred solution of 0.8 g of the ketone (V) in 40 ml of methanol, solutions of 2.1 g of iodine in 25 ml of methanol and of 4 g of caustic potash in 8 ml of water and 15 ml of methanol were added simultaneously in such a way that iodine was always present in excess. The addition was complete in 20 minutes, and the mixture was then set aside for two hours. The greater part of the methanol was distilled off under reduced pressure, and 10 ml of water was added. The solution was acidified to Congo red, and the precipitated yellow mass was extracted three times with ether. The ether extracts were carefully washed with a 10% thiosulfate solution until decolorized, and were then filtered. The ether was removed, and 5 ml of methanol and 4 ml of 30% caustic soda were added to the residue. The brown solution was heated under reflux for four hours in a water bath. The methanol was removed, and the residue was diluted with water (5 ml), extracted twice with ether to remove neutral products, and acidified with 20% hydrochloric acid (10 ml) cooled to −5°. After one hour the yellow precipitate formed was filtered off under suction and washed with ice water. Crystallization from 5 ml of acetic acid yielded 0.39 g (41%) of the acid (IX) in the form of a white powder, m.p. 199-202°.

Found %: C 71.75; 71.5; H 9.35; 9.25
$C_{20}H_{30}O_4$ Calculated %: C 71.85; H 9.05

Dehydrogenation of the Acid (IX)

A mixture of 0.33 g of the acid (IX), 8 ml of benzene, and 0.6 g of 10% palladized charcoal was heated in a rotating autoclave in an atmosphere of nitrogen (initial pressure 20 atm) at 350° for 11 hours. The reaction mixture was filtered, the benzene was distilled off, and the residue was dissolved in 1 ml of petroleum ether. The solution, on cooling, gave a crystalline precipitate, which was filtered off under suction and washed with petroleum ether. On account of its high solubility, only 10 mg of 2-ethyl-1-methylphenanthrene (X), m.p. 95-96°, could be isolated.

Found %: C 92.9; 92.9; H 7.2; 7.2
$C_{17}H_{16}$ Calculated %: C 92.7; H 7.3

The mother liquor, on being cooled to −70°, yielded a further 38 mg of hydrocarbon, m.p. 85-88°.

A solution of 22 mg of 2-ethyl-1-methylphenanthrene (X) of m.p. 85-88° in 1 ml of acetic acid was mixed with a solution of 50 mg of chromic anhydride in 1 ml of acetic acid. The mixture was heated at 100° for ten minutes, and then cooled. Water (1 ml) was added, and the mixture was heated until the turbidity present disappeared. It was then set aside to crystallize, and on the next day 10 mg of 2-ethyl-1-methyl-9,10-phenanthrenequinone (XI) came down. Crystallization from 0.5 ml of methanol yielded 4 mg of pure quinone (XI), m.p. 155-157°. The quinoxaline (XII), which was prepared by heating the quinone (XI) with o-phenylenediamine in methanol in the presence of a drop of acetic acid, is a yellow crystalline substance, m.p. 108-109° (from methanol).

Oxidation of the Ketone (XIII) and Dehydrogenation of the Acid Formed

The ketone (XIII) (1.2 g) was oxidized with iodine in alkaline solution, as described above. A dicarboxylic acid (450 mg) was obtained, and this was dehydrogenated under the conditions described above for 12 hours, yielding 48 mg of 2-ethyl-1-methylphenanthrene (X), m.p. 85-88°. Without further purification, this was oxidized with chromic anhydride in acetic acid, yielding 7 mg of the quinone (XI), m.p. 155-156°. The quinoxaline prepared from this quinone melted at 105-107°; the mixture melting point with the quinoxaline (XII) from the preceding experiment was not depressed.

Hydrogenation of the Diketones (IV A), (IV B), (IV C), and (IV D), in Presence of an Adams Platinum Catalyst

The diketones IV A, IV B, IV C, and IV D did not undergo hydrogenation in alcoholic solution in presence of an Adams platinum catalyst. When the diketone IV A was submitted to the hydrogenation treatment in acetic acid, it was not affected. When the diketones IV B, IV C, and IV D were hydrogenated in acetic acid (30-100 mg of diketone, 10-20 mg of PtO_2 3-5 ml of acetic acid; 3 hours), a noncrystallizing mixture was obtained in each case. Attempts to separate these mixtures chromatographically were not successful.

Hydrogenation of the Diketone IV A in Presence of Palladium on Barium Carbonate and Chloroplatinic Acid

A solution of 1.0 g of the diketone IV A of m.p. 166-167° in 10 ml of acetic acid was shaken in an atmosphere of hydrogen in presence of 0.5 g of $Pt/BaSO_4$ for one hour. No hydrogenation occurred; it began only when a few drops of a concentrated H_2PtCl_6 solution had been added. In the course of ten minutes, 150 ml of hydrogen (24°, 760 mm) was absorbed, and absorption then ceased. The solution was filtered, diluted with three times its volume of water, and extracted with benzene. The benzene extracts were washed with a 2% solution of caustic soda until neutral, and the benzene was removed under reduced pressure. A small amount of petroleum ether was added to the residual viscous liquid, and it then partially crystallized out, yielding 110 mg of white crystals, m.p. 147-149°. According to analysis, this was a mixture (or molecular compound) of the hydroxy ketone XVI and its acetic ester.

Found %: C 78.0; 77.7; H 9.7; 9.5
$C_{20}H_{30}O_2 + C_{20}H_{29}O(OCOCH_3)$. Calculated %: C 78.0 H 9.6

These crystals were dissolved in 2 ml of alcohol, and 0.2 ml of 10% NaOH was added. The mixture was heated for five minutes in a water bath and then diluted with an equal amount of water. Crystals of the hydroxy ketone XVI quickly made their appearance; they were filtered off under suction, washed with water, and vacuum-dried. The product was 60 mg of the hydroxy ketone XVI, m.p. 131-132°.

Found %: C 79.3; 79.4; H 10.2; 10.2
$C_{20}H_{30}O_2$. Calculated %: C 79.4; H 10.0

Oxidation of the Hydroxy Ketone XVI

A solution of 35 mg of the hydroxy ketone XVI in 0.4 ml of acetic acid was mixed with a solution of 9 mg of chromic anhydride in 0.8 ml of acetic acid, and the mixture was set aside for two days. The solution was diluted with three times its volume of water and extracted with ether. The ether extracts were shaken with caustic soda solution until neutral, and the ether was distilled off. In a short time the residue partially crystallized out, yielding 8 mg of crystals of the diketone IV D, m.p. 111-113°, undepressed by admixture of some of the diketone IV D obtained as described above.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-Dimethyl-2-cyclopenten-1-one (III)

A mixture of 12.0 g of the dienone II and 66 g of the dimethylcyclopentenone III was heated in an atmosphere of nitrogen in sealed tubes at 170° for 10 hours 30 minutes. Excess of the ketone III was then removed under reduced pressure in a water bath until crystallization set in (44 g was distilled over). Petroleum ether (10 ml) and benzene (1 ml) were added to the crystallizing residue, and after two hours the precipitated crystals were filtered off under suction and washed with a cold mixture of petroleum ether and benzene (10 : 1). The product was 4.1 g of pure diketone XVII A in the form of white needles, m.p. 187-189°. The mother liquor remaining after separation of these crystals was evaporated down, and 13 g of dimethylcyclopentenone was driven off under reduced pressure in a water bath; the residue was poured into a mixture of 10 ml of petroleum ether and 2 ml of benzene. A second crop of crystals was obtained, and after one hour these were filtered off under suction and washed with a mixture of petroleum ether and benzene (10 : 1), yielding 4.6 g of a crystalline powder, m.p. 144-159°. The second mother liquor was evaporated down, diluted with 10 ml of petroleum either, and set aside for one day. A third crop of crystals (0.4 g) was obtained; m.p. 155-190°. The third mother liquor was evaporated down, and unchanged dienone II was distilled off at a residual pressure of 0.5 mm, the bath temperature being not above 130° (1.6 g of dienone was obtained). The residue was dissolved in a mixture of 5 ml of petroleum ether and 1.5 ml of benzene, and was set aside at 0-3°. Crystals were very slowly precipitated, and after ten days this fourth batch of crystals was filtered off at the pump and washed with petroleum ether (1.0 g; m.p. 130-150°). In this way altogether 10.1 g of a mixture of crystalline isomers of 10,14,17-trimethyl-9(11)-cardosterene-2,15-dione was obtained, the yield being 53% on the amount of the dienone II taken for reaction, and 61% on the amount of the dienone II that reacted.

By fractional crystallization from a mixture of petroleum ether and benzene in conjunction with mechanical sorting of the crystals, the second batch of crystals yielded the diketone XVII A, m.p. 187-189°, and the diketone XVII B, m.p. 177-178°. In a similar way, the third batch of crystals gave the isomer XVII C, m.p. 199-200°, and the fourth batch of crystals yielded the isomers XVII B, m.p. 177-178°, and XVII D, m.p. 163-164°. Altogether, the following amounts were isolated in the pure state: 4.86 g of XVII A, 2.57 g of XVII B, 0.25 g of XVII C, and 0.16 g of XVII D.

The isomer XVII A: needles, m.p. 187-189°.

Found %: C 79.8; 79.6; H 9.6; 9.4
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

The isomer XVII B: large prisms, m.p. 177-178°.

Found %: C 80.1; 80.05; H 9.35; 9.4
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

The isomer XVII C: plates, m.p. 199-200°.

Found %: C 80.2; 80.2; H 9.4, 9.4
$C_{20}H_{28}O_2$ Calculated %: C 80.0; H 9.4

The isomer XVII D: cubes, m.p. 163-164°.

Found %: C 80.0; 80.2; H 9.45; 9.4
$C_{20}H_{28}O_2$ Calculated %: C 80.0; H 9.4

A mixture of XVII A and XVII B melted at 160-170°, and a mixture of XVII A and XVII C at 160-165°.

Isomerization of the Diketone XVII A

A mixture of 500 mg of the diketone XVII A of m.p. 187-189°, 10 ml of acetic acid, 20 ml of concentrated hydrochloric acid, and 10 ml of toluene was boiled under reflux for four hours. The toluene layer was separated, and the water layer was extracted with benzene. The united benzene-toluene extracts were neutralized by agitation with a 5% solution of caustic soda, the solvent was driven off under reduced pressure, and the dry residue was crystallized from alcohol, yielding 400 mg of unchanged diketone XVII A. By slow crystallization of the mother liquor in conjunction with mechanical selection of the crystals, it was found possible to isolate 70 mg of the isomeric diketone XVII E in the form of fine colorless plates, m.p. 139-141°.

Found %: C 80.0; H 9.5, 9.6
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Heating of the diketone XVII A in xylene at 170° for ten hours did not cause it to isomerize. Even the last batches of crystals from the mother liquor melted at 188-190°, and showed no depression in admixture with the original diketone XVII A.

Isomerization of the Diketone XVII B

The diketone XVII B of m.p. 177-178° (190 mg) was given the same isomerization treatment, but the boiling lasted ten hours. About 100 mg of the original diketone was recovered unchanged. By slow crystallization of the mother liquor and mechanical selection of crystals, about 20 mg of the isomeric diketone XVII F was isolated as colorless needles, m.p. 111-112°.

Found %: C 80.0; H 9.5
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Clemmensen Reduction of the Diketone XVII A

A mixture of 1.0 g of the diketone XVII A, m.p. 187-189°, 25 ml of acetic acid, 37 ml of concentrated hydrochloric acid, 15 ml of toluene, and 10 g of amalgamated zinc filings was boiled under reflux for five hours. The reaction mixture was diluted with 30 ml of water, the toluene layer was separated, and the water layer was extracted twice with benzene. The united extracts were neutralized by agitation with 10% caustic soda, and the solvent was removed under reduced pressure. The residue was dissolved in 3 ml of ether and set aside in the cold to crystallize; the solution yielded 0.12 g (14%) of crystals of the ketone V, m.p. 99-100°. Crystallization from alcohol raised the melting point to 101-102°. In admixture with the ketone V obtained by reduction of the diketone IV A it showed no depression in melting point. Its dinitrophenylhydrazone melted at 229-231° and showed no melting point depression in admixture with the dinitrophenylhydrazone of the ketone V obtained previously.

Clemmensen Reduction of the Diketone XVII C

Reduction of 80 mg of the diketone XVII C of m.p. 199-200°, carried out as above, yielded 10 mg of the ketone V, m.p. 103-104° (no depression with previously prepared ketone V).

Clemmensen Reduction of the Diketone XVII B

The reduction was performed similarly to that of the diketone XVII A. From 0.8 g of the diketone XVII B, m.p. 177-178°, 80 mg of the ketone XIII, m.p. 109-112° was obtained. Crystallization from a mixture of alcohol and petroleum ether gave crystals of m.p. 119-121°. A mixture melting point with the ketone XIII obtained previously from the diketone IV B was not depressed. The dinitrophenylhydrazone formed orange needles, m.p. 215-217°.

Clemmensen Reduction of the Diketone XVII D

Clemmensen reduction of the diketone XVII D of m.p. 163-164° (65 mg) was carried out as in the preceding examples. The reaction product did not crystallize even at -70°, and it was therefore dissolved in petroleum ether and chromatographed on aluminum oxide (1 g, length of column 6 cm). Only 5 mg of crystals, m.p. 78-80° (from a mixture of petroleum ether and benzene) could be obtained as a result of successive elution with petroleum ether, a mixture of petroleum ether and benzene, and benzene. The dinitrophenylhydrazone formed fine yellow needles, m.p. 198-201° (decomposition).

Hydrogenation of the Diketones XVII A, XVII B, and XVII C in Presence of an Adams Platinum Catalyst

The diketones XVII A, XVII B, and XVII C did not undergo hydrogenation in alcoholic solution in presence of an Adams platinum catalyst. When attempts were made to hydrogenate these diketones in acetic acid (60-100 mg of diketone, 15-20 mg of PtO_2 and 5 ml of acetic acid; 3 hours), the original diketone (20-30 mg) was in every case recovered unchanged.

SUMMARY

1. Total syntheses of steroid diketones of the cis-cis series have been performed by the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4 dimethyl-2-cyclopenten-1-one (III). In both cases a total yield of about 60% was obtained of a mixture of three or four isomeric steroid diketones having the A and B rings and the C and D rings united in the cis-configuration.

2. It has been shown that, irrespective of the presence and positions of substituents in the A ring, all steroid diketones synthesized by the diene-condensation method have the so-called "inverted" structure, i.e. the D ring has an angular methyl group in the 14-position and a carbonyl group in the 15-position. For some compounds the difference between the isomers lies in the difference in relative spatial positions of the A and B rings and of the C and D rings; and for other compounds it lies in the difference in the spatial disposition of the hydrogen at C-8.

3. It has been shown that the 9(11) double bond in tetracyclic steroid diketones migrates comparatively readily to the 8(9)-position under the action of hydrochloric acid.

4. It has been found that the keto group in the D ring is extremely stable under the conditions of Clemmensen reduction, tetracyclic steroid 2,15- and 3,15-diketones being converted into 15-monoketones.

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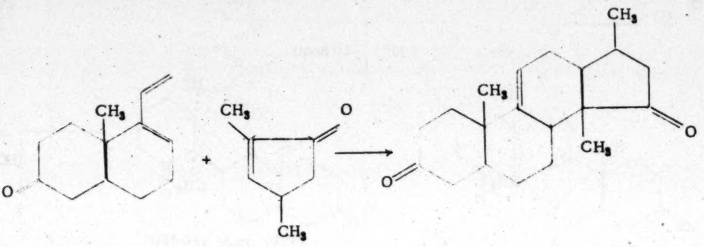
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

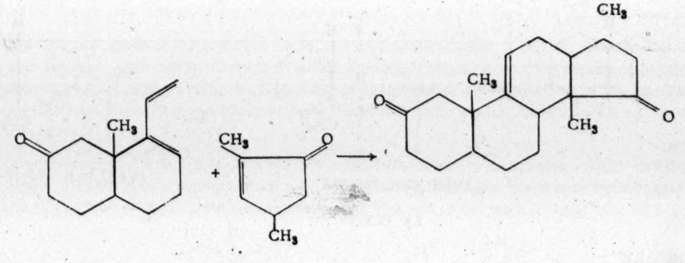
COMMUNICATION XIX. CONDENSATION OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE WITH 2-CYCLOHEXEN-1-ONES AND WITH CITRACONIC ANHYDRIDE

I. N. Nazarov, I. I. Zaretskaya, G. P. Verkholetova, and I. V. Torgov

In the preceding communication [1] we have described the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-dimethyl-2-cyclopenten-1-one. By this means we obtained a number of steroid diketones of the cis-cis series and having an "inverted" structure:



(I)



(II)

In the present investigation we have studied the condensation of the dienone I with 2-methyl-2-cyclohexen-1-one (III), with 2-cyclohexen-1-one (IV), with citraconic anhydride (V), and with p-benzoquinone, and also the condensation of the dienone II with 2-methyl-2-cyclohexen-1-one (III). When the dienone I was heated with ten times its amount of 2-methyl-2-cyclohexen-1-one (III) at 170° for ten hours, a 50% yield was obtained of a mixture of tetracyclic diketones of the cis-cis series, from which four isomers, VI A, VI B, VI C, and VI D, of 10,14-dimethylcardochrysanene-3,15-dione* were isolated in the proportions 40 : 10 : 5 : 1, approximately. In some experiments the proportion of the isomer VI D was considerably more, and that of the isomer VI A was correspondingly less.

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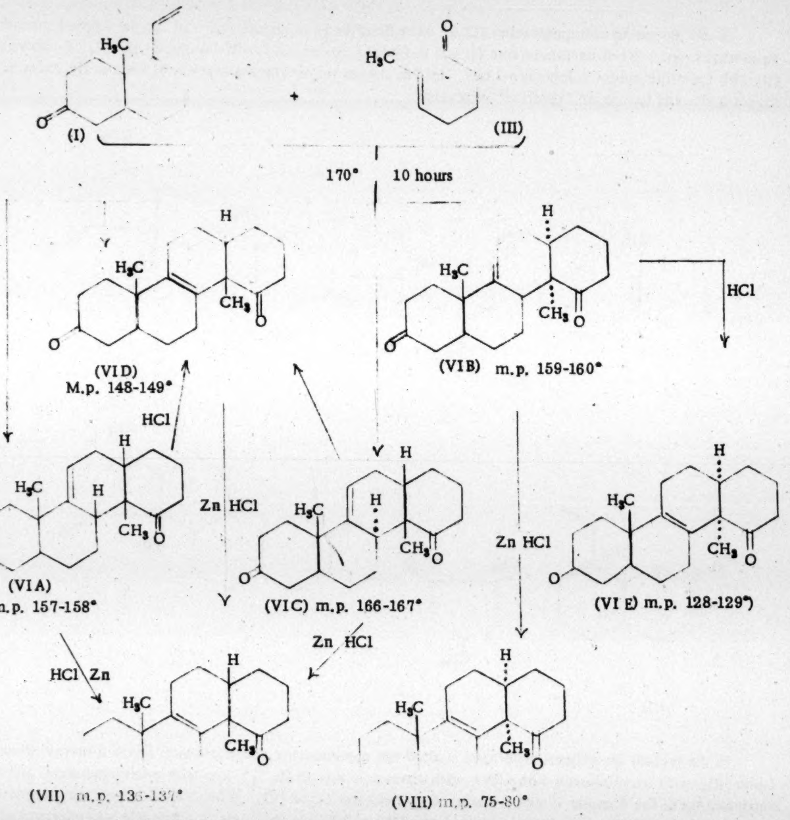
* Nazarov's nomenclature for synthetic steroids, see Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 726 (Consultants Bureau Translation, p 651).

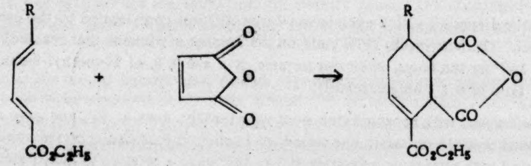
The difference between the isomers VI A and VI C lies in a difference in spatial disposition of the hydrogen atom at C-8, for, on being heated with hydrochloric acid, both isomers give the same isomer (VI D) with displacement of the double bond from the 9(11)- to the 8(9)-position, as shown in the preceding communication [1].

All three diketones, VI A, VI C, and VI D, give the same monoketone (VII) when subjected to Clemmensen reduction. Since it has been shown previously [1] that it is the keto group in the A ring that is removed in this reaction, the monoketone obtained must have the structure 10,14-dimethyl-8-cardochrysanene-15-one (VII). Reduction of the isomer VI B yields the monoketone VIII, which is distinct from the monoketone VII. If it is assumed, on analogy with the already studied reactions of the dienone I with 2-4-dimethyl-2-cyclopenten-1-one [1], that all of the isomers are of inverted structure, then the difference between the isomers VI B and VI A can only be explained by a difference in the spatial arrangement of the substituents at $C_{13}-C_{14}$.


H₃C
O
(I)
+
H₃C
O
(III)
170°
10 hours
H
H₃C
CH₃
O
O
(VI D)
M.p. 148-149°
H
H₃C
CH₃ O
O
(VI B) m.p. 159-160°
HCl
HCl
H
H₃C
H
CH₃ O
O
(VI A)
m.p. 157-158°
Zn HCl
H
H₃C
H
CH₃ O
O
(VI C) m.p. 166-167°
Zn HCl
H
H₃C
CH₃ O
O
(VI E) m.p. 128-129°
Zn HCl
HCl Zn
H
H₃C
CH₃ O
(VII) m.p. 136-137°
H
H₃C
CH₃ O
(VIII) m.p. 75-80°

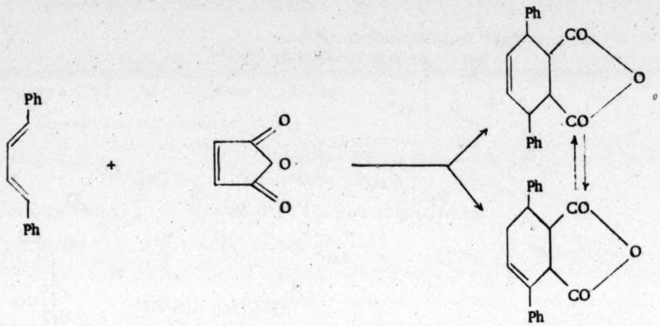
The fact that the isomer VI D is present in the reaction mixture shows that in the course of the diene synthesis the double bond is displaced from its original 9(11)-position to the 8(9)-position.

Such instances of the displacement of a double bond in the course of the diene synthesis are comparatively rare. In the condensation, however, of a sorbic or muconic ester with maleic anhydride, the double bond moves to the position of conjugation with the carboxyl [2]:



$R = CH_3, CO_2C_2H_5$

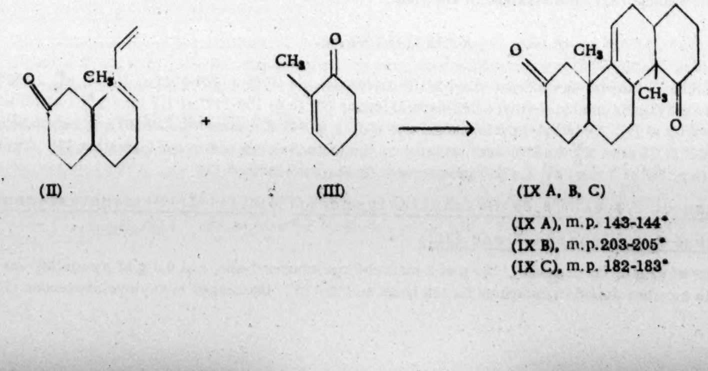
In the condensation, also, of 1,4-diphenyl-1,3-butadiene with maleic anhydride, a mixture of readily interconvertible isomers is obtained, and this is explained by the investigators as a displacement of the double bond [3]:



Similar phenomena in sorbic acid condensations have been observed also by Deno [4] and Alder [5]. We consider that the isomer VI D, being the most stable one, has an 8(9) double bond, whereas in the isomer VI A, which is formed in the greatest amount during the diene synthesis, the double bond is in the 9(11)-position.

The carbonyl group of the monoketone VII is exceptionally inert: it will not undergo Clemmensen reduction, and it does not react with methylmagnesium iodide or methyllithium, even after prolonged heating. This behavior is probably to be explained by steric hindrance due to the powerful screening effect of the 14-methyl group, and this indirectly confirms the correctness of our assumed "inverted" structure for the ketone VII and therefore the structure of the diketones VI A, VI C, and VI D.

Condensation of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclohexen-1-one (III) also gave a mixture of ketones, from which it was found possible to isolate three isomers, IX A, IX B, and IX C, of 10,14-dimethyl-9-cardochrysanene-2,15-dione in the proportions of 15 : 12 : 1 approximately.



(II)

(III)

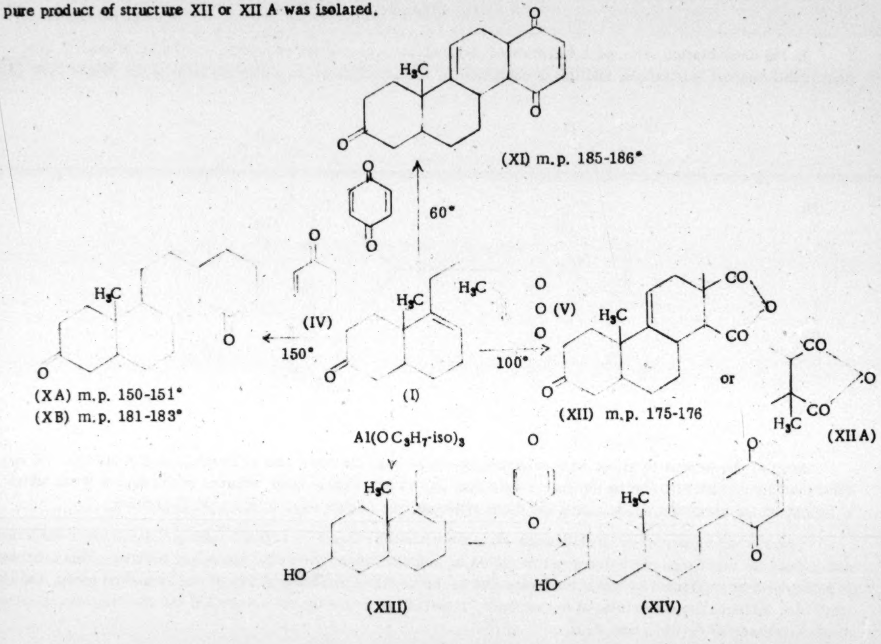
(IX A, B, C)

(IX A), m.p. 143-144°
(IX B), m.p. 203-205°
(IX C), m.p. 182-183°

Owing to the small amount available of the original dienone (II) and the small amounts obtained of the diketones IX, the latter were not investigated further.

The condensation of the dienone I with 2-cyclohexen-1-one (IV) was complicated by the great tendency of the latter to condense with itself. The best results (27% yield on the amount of dienone that reacted) were obtained by heating the components at 150° for ten hours, when two isomers, X A and X B, of 10-methyl-9-cardochrysanene-3,15-dione were obtained in the ratio of 6 : 1 approximately.

Condensation of the dienone I with benzoquinone went very readily, even at 60°, and gave a mixture of products, from which it was found possible to isolate one isomer of 10-methyl-9,16-cardochrysadiene-3,15,17a-trione (XI). Heating of the dienone I with citraconic anhydride (V) at 100° gave a mixture of anhydrides, from which a pure product of structure XII or XII A was isolated.



We have also reduced the dienone I with aluminum isopropoxide to the dienol XIII (a mixture, of course, of stereoisomers). This dienol (XIII) was condensed with 2,4-dimethyl-2-cyclopenten-1-one and with p-benzoquinone. In the first case no crystalline product could be isolated, and in the second case 10-methyl-9,16-cardochrysadien-3-ol-15,17a-dione (XIV) was obtained in low yield.

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm; n_D^{20} 1.5270) were previously described by us [6]. 2-Methyl-2-cyclohexen-1-one (III) (b.p. 56° at 9 mm; n_D^{20} 1.4865) and 2-cyclohexenone (IV) (b.p. 63° at 20 mm; n_D^{20} 1.4872) were prepared by the method developed in our laboratory [7]. Citraconic anhydride (V) (b.p. 80° at 7 mm; n_D^{20} 1.4720) was prepared by Shriner's method [8].

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Methyl-2-cyclohexen-1-one (III)

A mixture of 12 g of the dienone I, 120 g of 2-methyl-2-cyclohexen-1-one, and 0.1 g of pyrogallol was heated in glass tubes in a carbon dioxide atmosphere for ten hours at 170-175°. Unchanged methylcyclohexenone (114 g) and dienone (4.5 g) were distilled off under reduced pressure, and the residue was dissolved with heat in 15 ml of petroleum ether. Crystallization rapidly set in, yielding 4.5 g of a crystalline mixture, m.p. 124-150°. After three days a further 1.05 g of mixture had separated from the mother liquor. The unchanged dienone was again treated with methylcyclohexenone under the same conditions, and 0.8 g of the crystalline mixture and 2.75 g of the dienone I were isolated.

Distillation of the mother liquors from the two experiments at 0.5 mm yielded 5.0 g of a viscous liquid, b.p. 160-170°, and this partially crystallized out when diluted with petroleum ether, yielding 1.4 g of crystals. The total amount of crystals obtained was 7.95 g, i.e., 42% on the total amount of dienone I taken, and 55% on the amount that reacted. The isomers were separated by fractional crystallization from a mixture of petroleum ether and benzene:

Isomer VI A, m.p. 157-158°, 1.2 g.

Found %: C 79.95; 79.7; H 9.4; 9.3
$C_{20}H_{28}O_2$. Calculated %: C 80.0 H 9.4

Isomer VI B, m.p. 159-160°, 0.35 g.

Found %: C 80.0; 80.05; H 9.4; 9.35
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

A mixture of VI A and VI B melted at 130-138°.

Isomer VI C, m.p. 166-167°, 0.17 g.

Found %: C 80.0; 79.9; H 9.3; 9.4
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

A mixture with VI A melted at 130-140°, and with VI B at 130-140°.

Isomer VI D, m.p. 148-149°, 30 mg.

Found %: C 79.9; 80.1; H 9.6; 9.5
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Mixtures with VI A and with VI B melted at 125-130°.

Attempt to Effect the Thermal Isomerization of the Diketones VI A – D

Samples of the diketones were heated in capillaries at 200° for one hour. The substances were greatly resinified, and on cooling only the isomer VI D partially crystallized. The crystals melted at 146-147°, i.e., the isomer VI D had not undergone thermal isomerization.

Isomerization of the Diketone VI A

A mixture of 110 mg of the diketone VI A, m.p. 157-158°, 3 ml of acetic acid, 3 ml of concentrated hydrochloric acid, and 5 ml of toluene was heated under reflux for nine hours. The toluene layer was separated, neutralized by agitation with 4% caustic soda, and filtered. The solvents were distilled off under reduced pressure, and the residue was crystallized from a mixture of benzene and petroleum ether (1 : 4), yielding 86 mg of the diketone VI D, m.p. 146-147°. A mixture melting point with the diketone VI D isolated after the condensation reaction was not depressed.

Isomerization of the Diketone VI C

The isomerization of the diketone VI C was performed similarly: from 35 mg of VI C, m.p. 166-167°, 5 mg of the diketone VI D, m.p. 145-146°, was obtained. In admixture with samples of the diketone VI D obtained above, there was no depression of melting point.

Isomerization of the Diketone VI B

The isomerization was performed in a similar manner: from 65 mg of the diketone VI B, m.p. 159-160°, 10 mg of the diketone VI E, m.p. 128-129° (from alcohol), was obtained.

Found %: C 79.5; 79.7; H 9.3; 9.5
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Attempt to Effect the Isomerization of the Diketone VI D

The isomerization treatment was carried out similarly on the diketone VI D: from 60 mg of the diketone VI D, m.p. 148-149°, 45 mg of the original diketone, m.p. 146-147°, was obtained after the usual treatment. The mixture melting point test showed no depression.

Clemmensen Reduction of the Diketone VI A

A mixture of 500 mg of the diketone VI A, m.p. 157-158°, 5 ml of toluene, 6 ml of acetic acid, 6 ml of concentrated hydrochloric acid, and 2.5 g of amalgamated zinc was boiled under reflux for four hours. The toluene layer was separated, neutralized by agitation with a 10% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the solid residue was crystallized from petroleum ether, yielding 303 mg (63%) of the monoketone VII as colorless plates, m.p. 136-137°.

Found %: C 84.0; 83.9; H 10.6; 10.6
$C_{20}H_{30}O$. Calculated %: C 83.85; H 10.6

Clemmensen Reduction of the Diketone VI C

The reduction was performed in a similar manner: from 26 mg of the diketone, m.p. 166-167°, 7 mg of the ketone VII, m.p. 135-136° was obtained. In admixture with the sample of ketone obtained in the previous experiment it showed no melting point depression.

Clemmensen Reduction of the Diketone VI D

The reduction was performed in a similar manner: from 200 mg of the diketone VI D, m.p. 148-149°, 106 mg of the ketone VII, m.p. 135-136°, was obtained. In admixture with samples of ketones from the preceding experiments there was no depression in melting point.

Clemmensen Reduction of the Diketone VI B

The reduction was performed in a similar manner: from 250 mg of the diketone VI B, m.p. 159-160°, after the usual treatment and one crystallization, 130 mg of a substance of m.p. 70-80° was obtained. Recrystallization gave 75 mg of the ketone VIII, m.p. 75-80°. Further crystallizations did not raise the melting point and did not make the melting range any narrower.

Found %: C 84.8; H 10.7
$C_{20}H_{30}O$. Calculated %: C 83.85; H 10.6

The high carbon content indicates that the ketone was contaminated by a hydrocarbon which could not be separated by crystallization.

Action of Methylmagnesium Bromide and Methyllithium on the Ketone VII

A solution of 230 mg of the ketone VII, m.p. 136-137°, in a mixture of 6 ml of ether and 1 ml of benzene was added to a Grignard reagent prepared from 0.2 g of magnesium, 1.2 g of methyl iodide, and 10 ml of ether. The reaction mixture was boiled for 15 minutes, cooled, and decomposed with ice. The ether layer was separated, the ether was removed, and the residue was crystallized from ether, yielding 150 mg of unchanged ketone VII, m.p. 136-137°. A mixture melting point with the original ketone was not depressed. When the reaction was carried out at 100° in toluene, 30 mg of the ketone VII was recovered from 170 mg taken, and the residue was a noncrystallizing mass. Similar results were obtained when methyllithium was used.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-Methyl-2-cyclohexen-1-one (III)

A mixture of 2.0 g of the dienone II and 5 g of 2-methyl-2-cyclohexen-1-one (III) was heated in a carbon dioxide atmosphere in a sealed glass tube for 13 hours at 170-175°. Methylcyclohexenone (4.1 g) was distilled off, and the residue was diluted with twice its volume of methanol and set aside to crystallize. After one week the crystals that had formed (0.3 g; m.p. 135-155°) were separated mechanically into a low-melting (141-143°) fraction and a high-melting (178-179°) fraction. After standing for two days the mother liquor yielded a second crop of crystals (0.2 g), m.p. 194-199°. Three isomers were isolated by crystallization from methanol.

Isomer IX A, prisms of m.p. 143-144° (corr.), 130 mg.

Found %: C 79.8; 79.7; H 9.5; 9.4
$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Isomer IX B, fine plates of m.p. 203-205° (corr.), 100 mg.

Found %: C 79.9; 79.7; H 9.4; 9.65

$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Isomer IX C, needles of m.p. 182-183°, 8 mg.

Found %: C 79.6; 79.7; H 9.4; 9.3

$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Cyclohexen-1-one (IV)

A mixture of 5.5 g of the dienone I, 40 g of 2-cyclohexen-1-one (IV), and 40 mg of pyrogallol was heated in an atmosphere of carbon dioxide in a sealed glass tube at 150° for ten hours. Unchanged cyclohexenone (35.5 g) and dienone (1.6 g) were distilled off, and the residue was mixed with 8 ml of petroleum ether and set aside for one day to crystallize. A crystalline mixture of m.p. 137-145° was obtained. The yield was 1.05 g, i.e., 17% on the total amount of dienone taken, or 27% on the amount that reacted. Two isomers, X A and X B, were isolated by means of crystallization from a mixture of petroleum ether and benzene (5 : 1).

Isomer X A, plates of m.p. 150-151°, 0.3 g.

Found %: C 79.6; 79.7; H 9.1; 9.2

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomer X B, needles of m.p. 181-183°, 50 mg.

Found %: C 79.4; 79.4; H 9.3; 9.3

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with p-Benzoquinone

A solution of 1 g of the dienone I and 0.55 g of benzoquinone, m.p. 115°, in 10 ml of absolute dioxane was heated in a carbon dioxide atmosphere in a glass tube at 60° for 4 hours 30 minutes. The dioxane was removed, and the residue was diluted with 6 ml of petroleum ether and 1 ml of benzene. The solution yielded 0.85 g (55%) of a mixture of crystals, and recrystallization from a mixture of petroleum ether and benzene yielded 0.12 g of pure triketone (XI) in the form of large yellowish scales, m.p. 185-186°.

Found %: C 76.2; 76.5; H 7.5; 7.6

$C_{19}H_{22}O_3$. Calculated %: C 76.5; H 7.4

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with Citraconic Anhydride (V)

A solution of 1.9 g of the dienone I and 1.1 g of citraconic anhydride (V) in 5 ml of benzene was heated in a carbon dioxide atmosphere in presence of traces of Methylene Blue in a glass tube at 100° for six hours. Benzene was removed under reduced pressure, and the viscous mass that remained partially crystallized when ether was added thus yielding 0.91 g of a crystalline mixture. The mixture was boiled with 20 ml of petroleum ether, and the undissolved crystals were separated and washed with petroleum ether. The product was 140 mg of the tricyclic anhydride XII or XII A, m.p. 175-176°.

Found %: C 71.6; 71.75; H 7.3; 7.3

$C_{18}H_{22}O_4$. Calculated %: C 71.5; H 7.3

Crystals of m.p. 150-160° separated from the mother liquor; these consisted of a mixture of isomers, and it was not found possible to separate them.

Reduction of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) to 1,2,3,4,4a,7,8,8a-Octahydro-4a-methyl-5-vinyl-2-naphthol (XIII)

A mixture of 5.2 g of the dienone I and 50 ml of a molar solution of distilled aluminum isopropoxide in isopropyl alcohol was distilled from a flask fitted with an efficient column so that distillation was at 6-8 drops per minute. After three hours' boiling, the distillate no longer gave a test for acetone (with dinitrophenylhydrazine). Boiling was continued for a further 30 minutes, and the bulk of the isopropyl alcohol was then distilled off under reduced pressure. The viscous mass that remained was decomposed by addition, under cooling, of 90 ml of 6% hydrochloric acid, and it was then extracted three times with ether. The ether extract, on standing, yielded 0.3 g of crystals, m.p. 183-200°. Crystallization from benzene gave a substance of m.p. 208-209°, corresponding to the formula $C_{13}H_{22}O_2$.

Found %: C 73.9; H 11.1

$C_{13}H_{22}O_2$. Calculated %: C 74.3; H 10.5

When the ether was removed, a viscous mass remained, and this, after dilution with 4 ml of petroleum ether and cooling, yielded 0.5 g of crystals, m.p. 155-157°. Crystallization from a mixture of petroleum ether and benzene (1 : 4) gave a substance of m.p. 160-161°, also of formula $C_{13}H_{22}O_2$.

Found %: C 74.3; H 10.4

$C_{13}H_{22}O_2$. Calculated %: C 74.3; H 10.5

The structures of these two crystalline compounds have not been established.

The filtrate obtained after separation of the crystals was vacuum-distilled, and yielded 3 g (50%) of 1,2,3,4,-4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol (XIII) as a viscous liquid, b.p. 120-121.5° at 1.5 mm, n_D^{20} 1.5293.

Found %: C 80.4; 80.5; H 10.6; 10.55

$C_{13}H_{20}O$. Calculated %: C 81.2; H 10.5

Condensation of 1,2,3,4,4a,7,8,8a-Octahydro-4a-methyl-5-vinyl-2-naphthol (XIII) with p-Benzoquinone

A solution of 0.8 g of the dienol XIII and 0.45 g of benzoquinone in 8 ml of dioxane was heated in a carbon dioxide atmosphere in a glass tube for five hours at 60°. The dioxane was removed under reduced pressure, and the residue was diluted with petroleum ether, when it partially crystallized, yielding 0.40 g (32%) of crystals of m.p. 128-130°. Two crystallizations from benzene gave the pure hydroxy diketone (XIV), m.p. 130-131°.

Found %: C 76.0; 76.0; H 8.0; 8.1

$C_{19}H_{24}O_3$. Calculated %: C 76.0; H 8.05

Condensation of the dienol XIII with 2,4-dimethyl-2-cyclopenten-1-one at 170° and at 140° gave noncrystallizing mixtures of products. It was not found possible to resolve them by chromatography.

SUMMARY

1. The total syntheses of some D-homosteroid diketones of the cis-cis series having a 15-keto group have been effected by condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-methyl-2-cyclohexen-1-one (III). Four isomeric tetracyclic ketones have been isolated, and of these two, VI A and VI C, differ only in the spatial disposition of the hydrogen at C_8, the third, VI D, differs in the position of the double bond (8- instead of 9-), and the fourth (VI B) differs from the other three in the spatial arrangement of the substituents at $C_{13}-C_{14}$.

2. It has been shown that in the course of the diene condensation the double bond may be displaced from the 9(11)- to the 8(9)-position.

3. When the steroid diketones are subjected to Clemmensen reduction, only the keto group in the ring A is removed, and the diketone is converted into a 15-monoketone.

4. Condensation of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclohexen-1-one (III) yielded three isomeric steroid diketones, IX A, IX B, and IX C. Condensations of 3,4,4a,-7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-cyclohexen-1-one, p-benzoquinone, and citraconic anhydride have also been carried out, and the compounds X, XI, and XII have been obtained.

5. Reduction of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with aluminum isopropoxide yielded 1,2,3,4,4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol (XIII), which, on being condensed with

p-benzoquinone, yielded the tetracyclic hydroxy diketone XIV.

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* See Consultants Bureau Translation, p. 799.

** See Consultants Bureau Translation, p. 69.

*** See Consultants Bureau Translation, p. 787.

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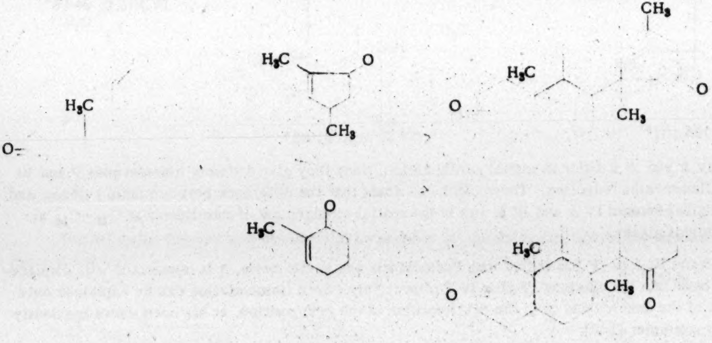
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XX. CONDENSATION OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE WITH 2-CYCLOPENTEN-1-ONE, 2-METHYL-2-CYCLOPENTEN-1-ONE, AND 3,5-DIMETHYL-3-CYCLOPENTENE-1,2-DIONE

I. N. Nazarov, G. P. Verkholetova, I. V. Torgov,

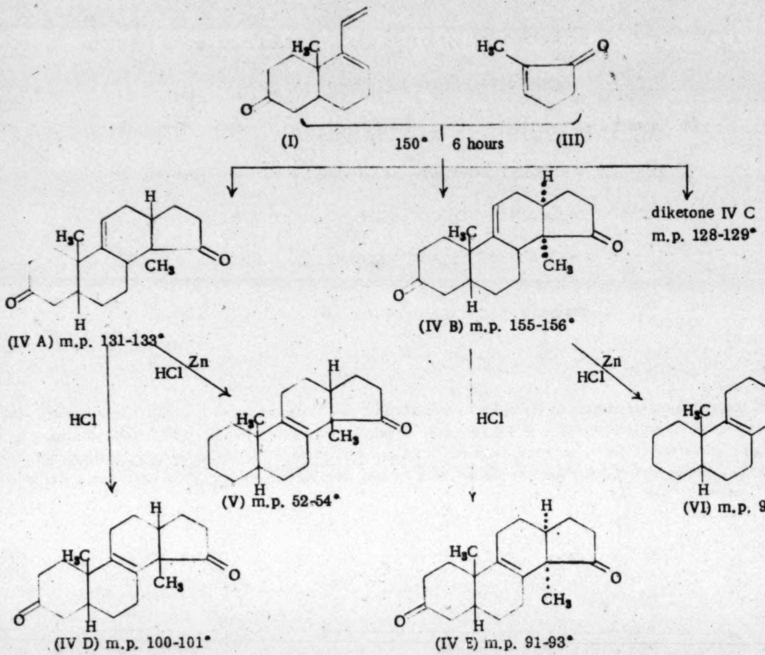
I. I. Zaretskaya, and S. N. Ananchenko

In the preceding communications [1, 2] we have described the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with various α,β-unsaturated cyclic ketones. As a result we have obtained a number of tetracyclic diketones of the cis-cis series, which have the fundamental skeleton of natural steroids, but have in most cases the so-called "inverted" structure:



Particular interest is presented by the synthesis of steroid diketones having a cyclopentane D ring (and no methyl group in the 17-position), since they are closest in composition and structure to natural hormones. In the present investigation, therefore, we have studied the condensation of dienones I and II with 2-methyl-2-cyclopenten-1-one (III), and have established the structures of the isomeric steroid diketones so obtained. It was found that in both cases the main products were again of the "inverted" structure.

The condensation of the dienones I and II with 2-methyl-2-cyclopenten-1-one did not go as well (30-35% yield) as the previously described condensation of these dienones with 2,4-dimethyl-2-cyclopenten-1-one (50-60% yield). The yield was reduced as a result of the high tendency of 2-methyl-2-cyclopenten-2-one to undergo self-condensation. Thus, when it is heated at 170° for three hours, it is completely converted into a viscous mixture of polymeric products, whereas 2,4-dimethyl-2-cyclopenten-1-one is practically unaffected under these conditions. The best results were obtained by heating the dienone I with double its quantity of 2-methyl-2-cyclopenten-1-one (III) at 150° for six hours. A 30% yield was then obtained of a mixture of tetracyclic diketones, from which three isomers, IV A, IV B, and IV C, of 10-14-dimethyl-9-cardosterene-3,15-dione* were isolated, the last in an impure state. The first two isomers, as will be shown below, were of the "inverted" structure. We therefore have the same picture as in the condensation of the dienone I with 2,4-dimethyl-2-cyclopenten-1-one, in which three isomers were also obtained, these having steroid skeletons with an inverted D ring.


H$_3$C
O
H$_3$C
O
(I)
150°
6 hours
(III)
H
H$_3$C
CH$_3$
O
O
H
(IV A) m.p. 131-133°
H
H$_3$C
O
CH$_3$
O
H
(IV B) m.p. 155-156°
diketone IV C
m.p. 128-129°
Zn
HCl
HCl
H
H$_3$C
CH$_3$
O
H
(V) m.p. 52-54°
HCl
Zn
HCl
H
H$_3$C
O
CH$_3$
H
(VI) m.p. 94-95°
H
H$_3$C
CH$_3$
O
O
H
(IV D) m.p. 100-101°
H
H$_3$C
O
CH$_3$
O
H
(IV E) m.p. 91-93°

The isomers IV A and IV B differ in spatial configuration, since they give different monoketones V and VI when subjected to Clemmensen reduction. There can be no doubt that the difference between these ketones, and also between the original ketones IV A and IV B, lies in the spatial arrangement of substituents at $C_{13}-C_{14}$ as indicated in the formulas given.

When the diketone IV A or IV B is boiled with hydrochloric and acetic acids, it is isomerized with displacement of the double bond into the diketone IV D or IV E respectively. Such isomerization can be explained only by the displacement of the double bond from the 9(11)-position to the 8(9)-position, as has been shown previously on the basis of many examples [1, 2].

The establishment of the structure of the ketones V and VI presented great difficulties. The method of oxidation with iodine in an alkaline medium with subsequent dehydrogenation of the acid formed into a phenanthrene derivative, which has given a positive result in other cases [1], was unsuitable in this case, since both possible structures, "normal" and "inverted", would give the same product, 1,2-dimethylphenanthrene. It appeared to be possible to convert the ketone V or VI into the corresponding alcohol by the action of methylmagnesium bromide, and then to convert the alcohol by dehydration, hydrogenation, and dehydrogenation into a 16,17-dihydromethylcyclopenta[a]phenanthrene described in the literature:

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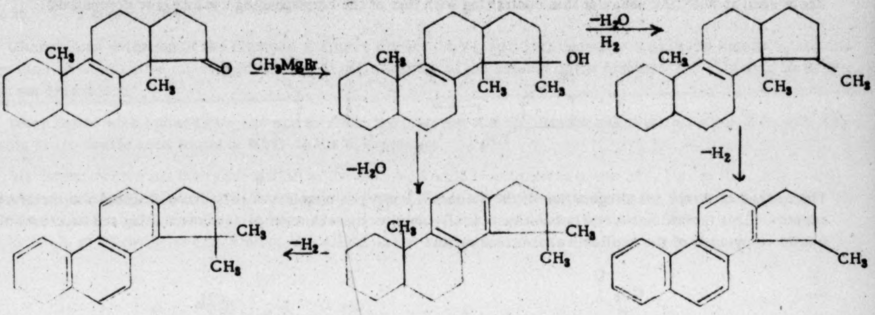
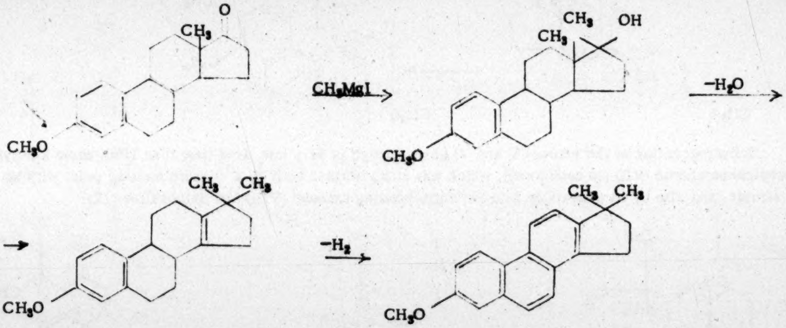
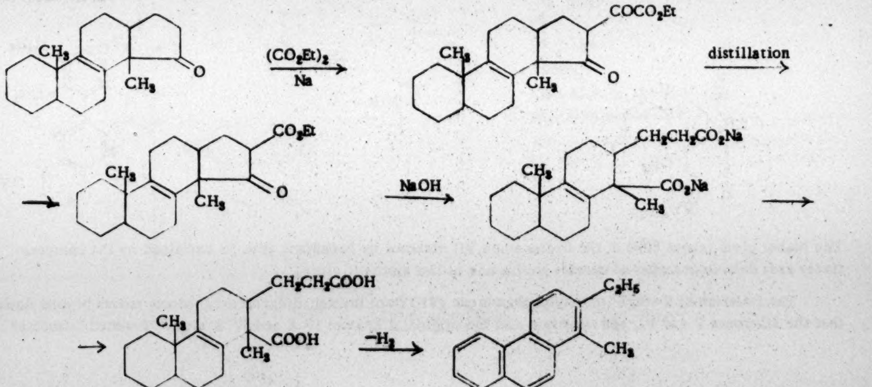
* Nazarov's nomenclature for synthetic steroids; see Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 726 (Consultants Bureau Translation, p 651).


CH₃
CH₃
O
CH₃MgBr
CH₃
OH
CH₃
CH₃
−H₂O
H₂
CH₃
CH₃
CH₃
−H₂O
−H₂
CH₃
CH₃
−H₂
CH₃
CH₃
CH₃
CH₃

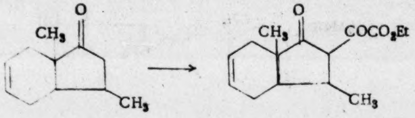
This method, however, was subject to doubt for two reasons. In the first place, the keto group in the D ring is very inert to the Grignard reagent, as we have shown in the preceding communication [2] in the case of a D-homosteroid diketone. In the second place, in the dehydration, a retro-pinacolin rearrangement may very well occur, which would lead to the unknown 16,17-dihydro-15,15-dimethylcyclopenta[a]phenanthrene. A similar example is found in the behavior of the methyl ether of estrone [3]:


O
CH₃
CH₃O
CH₃MgI
CH₃
OH
CH₃
CH₃O
−H₂O
CH₃
CH₃
CH₃O
−H₂
CH₃
CH₃
CH₃O

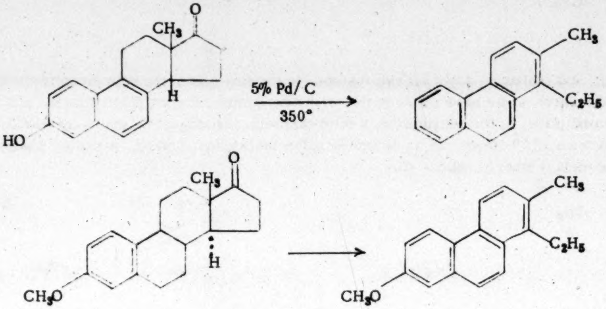
The following method also appeared to be possible for the determination of the structure of the steroid ketones V and VI:


CH₃
CH₃
O
(CO₂Et)₂
Na
COCO₂Et
CH₃
CH₃
O
distillation
CO₂Et
CH₃
CH₃
O
NaOH
CH₂CH₂CO₂Na
CH₃
CO₂Na
CH₃
CH₂CH₂COOH
CH₃
COOH
CH₃
−H₂
C₂H₅
CH₃

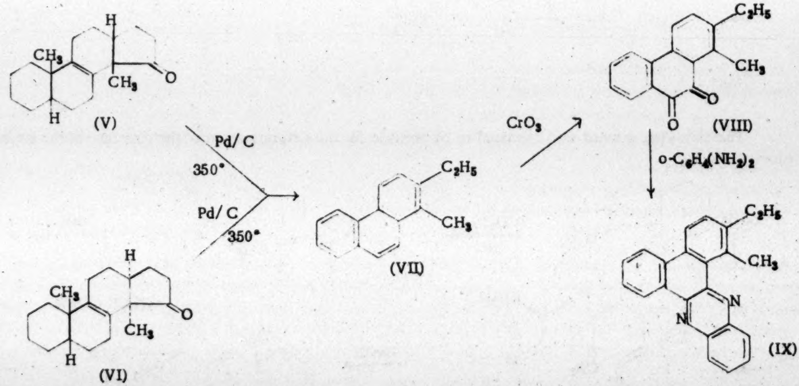
However, preliminary experiments on 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone, taken as a model example, showed that although condensation with oxalic ester proceeded readily, the elimination of carbon monoxide did not occur even at 200° (the behavior thus contrasting with that of the corresponding cyclohexane compounds):


O
CH_3
CH_3
O
CH_3
$COCO_2Et$
CH_3

The method of direct dehydrogenation of the ketones V and VI in presence of palladized charcoal was therefore adopted. This method has recently been successfully applied by Bachmann [4] for determining the structures of steroid compounds of the equilenin and estrone series:


O
CH_3
H
HO
5% Pd/C
350°
CH_3
C_2H_5
O
CH_3
H
CH_3O
CH_3
C_2H_5
CH_3O

Dehydrogenation of the ketones V and VI gave, though in very low yield (less than 10%), some 2-ethyl-1-methylphenanthrene (VII) (in both cases), which was characterized both by a mixture melting point with an authentic sample, and also by its conversion into the corresponding quinone (VIII) and quinoxaline (IX):


H
CH_3
CH_3
O
H
(V)
Pd/C
350°
Pd/C
350°
C_2H_5
CH_3
(VII)
H
CH_3
O
CH_3
H
(VI)
CrO_3
C_2H_5
CH_3
O
O
(VIII)
$o\text{-}C_6H_4(NH_2)_2$
C_2H_5
CH_3
N
N
(IX)

The higher yield (about 80%) of the hydrocarbon VII obtained by Bachmann is to be explained by the comparatively easy dehydrogenation of steroids having one or two aromatic rings.

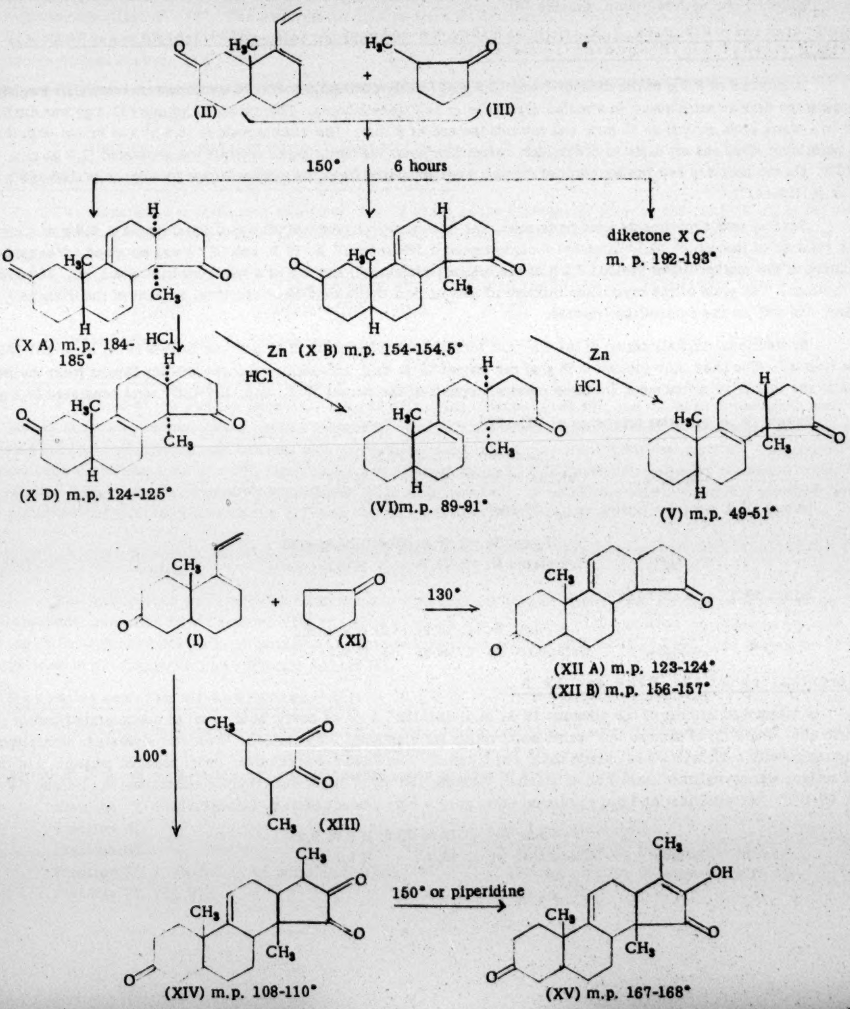
The isolation of 2-ethyl-1-methylphenanthrene (VII) from the dehydrogenation products proves beyond doubt that the diketones V and VI, and therefore also the original diketones IV A and IV B, are of "inverted" structure.

Condensation of the dienone II with 2-methyl-2-cyclopenten-1-one (III), carried out under the same conditions, gave a 38% yield of a mixture of three isomers, X A, X B, and X C, of 10-14-dimethyl-9-cardosterene-2,15-dione in the proportions of 25 : 7 : 1 approximately.

Clemmensen reduction of the diketone X A gave the ketone VI, and the diketone X B gave the ketone V, and in this way their structures were established. Owing to the smallness of the amount of the diketone X C obtained, its structure was not determined.

When boiled with hydrochloric and acetic acids, the diketone X A was isomerized to the diketone X D, with displacement of the double bond from the 9(11)- to the 8(9)-position.

We further carried out the condensation of the dienone I with 2-cyclopenten-1-one (XI), but, as the latter is still more sensitive to heating than 2-methyl-2-cyclopenten-1-one (III), it was necessary to lower the temperature to 130°. An 11%yield was obtained of a crystalline mixture of isomers, from which it was found possible to isolate two isomers, XII A and XII B, of 10-methyl-9-cardosterene-3,15-dione in the pure state.



(II)

(III)

diketone X C
m. p. 192-193°

(X A) m.p. 184-185°

(X B) m.p. 154-154.5°

(X D) m.p. 124-125°

(VI)m.p. 89-91°

(V) m.p. 49-51°

(I)

(XI)

(XII A) m.p. 123-124°
(XII B) m.p. 156-157°

(XIII)

(XIV) m.p. 108-110°

(XV) m.p. 167-168°

When the dienone I was condensed with 3,5-dimethyl-3-cyclopentene-1,2-dione (XIII) at 100°, a 14% yield of 10,14,17-trimethyl-9-cardosterene-3,15,16-trione (XIV) was obtained. The latter, even by simple fusion, is very readily isomerized into 10,14,17-trimethyl-9,16-cardosteradien-16-ol-3,15-dione (XV), the enol form of the triketone XIV. The same transformation can be effected also by the action of piperidine. If the condensation of the dienone I with the diketone XIII is carried out at 120°, it is not possible to isolate any triketone XIV; only the hydroxy diketone XV is obtained. We have previously observed similar cases of the ready isomerization of cyclic 1,2-diones into enolones [5].

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm; n_D^{20} 1.5270) were prepared by the method described previously [6]. 2-Methyl-2-cyclopenten-1-one (III) (b.p. 52-53° at 15 mm; n_D^{20} 1.4770) and 2-cyclopenten-1-one (XI) (m.p. 45° at 15 mm; n_D^{20} 1.4700) were prepared by the method developed in our laboratory [7]. 3,5-Dimethyl-3-cyclopentene-1,2-dione (XIII) (m.p. 66-67°) was prepared by the oxidation of 2,4-dimethyl-2-cyclopenten-1-one with selenium dioxide [8].

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 6.9 g of the dienone I and 13.8 g of freshly distilled 2-methyl-2-cyclopenten-1-one (III) was heated in a carbon dioxide atmosphere in a sealed glass tube at 150° for six hours. The excess of ketone (11.4 g) was distilled off in a water bath, at first at 15 mm, and towards the end at 2 mm. The viscous residue (8.2 g) was mixed with 7 ml of petroleum ether and set aside to crystallize. After five hours the first crop of crystals was separated (1.3 g; m.p. 117-120°). On the next day two further crops of crystals were separated from the mother liquor (0.65 g, m.p. 103-108°; 0.2 g, m.p. 125-141°).

Several such experiments were performed, and from a total amount of 22.4 g of the dienone I, 6.9 g of a crystalline mixture of isomers of 10,14-dimethyl-9-cardosterene-3,15-dione (IV A, IV B, and IV C) was obtained. Vacuum distillation of the mother liquor yielded 7.2 g of the original dienone (I) and 5 g of a noncrystallizing oil, b.p. 160-170° at 0.5 mm. The yield of the crystalline mixture of isomers was therefore 20% on the total amount of the dienone I taken, and 30% on the amount that reacted.

By fractional crystallization of the first and second crops of crystals, 2.75 g of the isomer IV A, m.p. 131-133°, was isolated. The third crop yielded 0.35 g of the isomer IV B, m.p. 155-156°. After the mother liquors from the isolation of the isomer IV A had stood for three months, crystals of the isomer IV C, m.p. 127-128°, were separated (0.2 g).

Isomer IV A, irregular prisms, m.p. 131-133°.

Found %: C 79.4; 79.5; H 9.3; 9.1
$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomer IV B, irregular prisms, m.p. 155-156°.

Found %: C 79.8; 79.8; H 9.3; 9.25
$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomer IV C, m.p. 127-128°.

Found %: C 78.2; 78.2; H 9.0; 9.1
$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomerization of the Diketone IV A

A mixture of 225 mg of the diketone IV A, m.p. 131-132°, 5 ml of acetic acid, 5 ml of concentrated hydrochloric acid, and 6 ml of toluene was boiled under reflux for nine hours. The toluene layer was separated, neutralized, by agitation with a 4% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the solid residue was crystallized from 1 ml of alcohol, yielding 195 mg of 10,14-dimethyl-8-cardosterene-3,15-dione (IV D), m.p. 97-100°. Recrystallization from petroleum ether gave a pure product of m.p. 100-100.5°.

Found %: C 79.5; 79.6; H 9.0; 9.2
$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomerization of the Diketone IV B

The isomerization was performed as above: from 187 mg of the diketone IV B, m.p. 155-156°, after the usual treatment of the reaction mixture and successive crystallizations from petroleum ether and alcohol, 29 mg of the diketone IV E, m.p. 91-93°, was obtained.

Found %: C 79.65; 79.7; H 9.3; 9.0
$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

In admixture with the diketone IV D it showed a strong depression in melting point (melted at 80-85°).

Clemmensen Reduction of the Diketone IV A

A mixture of 1 g of the diketone IV A, m.p. 131-133°, 17 ml of acetic acid, 17 ml of concentrated hydrochloric acid, 17 ml of toluene, and 6.5 g of amalgamated zinc was boiled under reflux for seven hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the noncrystallizing residue was dissolved in 2 ml of petroleum ether and set aside to crystallize at −70°. The precipitated crystals were washed twice by decantation with petroleum ether, and were dried in a desiccator. The product was 0.35 g of 10,14-dimethyl-8-cardosteren-15-one (V) in the form of white, poorly defined crystals, m.p. 53-54°.

Found %: C 84.3; 84.2; H 10.5; 10.4
$C_{19}H_{28}O$. Calculated %: C 83.8; H 10.3

The dinitrophenylhydrazone formed orange needles, m.p. 193-194° (corr.).

Clemmensen Reduction of the Diketone IV B

The reduction was performed as above: from 300 mg of the diketone IV B, m.p. 155-156°, 80 mg of the ketone VI, m.p. 88-91°, was isolated. Crystallization from 1 ml of petroleum ether (at −70°) gave 55 mg of pure ketone VI, m.p. 94-95°.

Found %: C 83.3; 83.3; H 10.15; 10.15
$C_{19}H_{28}O$. Calculated %: C 83.8; H 10.3

The dinitrophenylhydrazone formed orange needles, m.p. 191-193°.

Dehydrogenation of the Ketone V

A mixture of 2.5 g of the ketone V, 3.3 g of palladized charcoal (10% Pd), and 30 ml of dry benzene was heated in a nitrogen atmosphere (initial pressure 25 atm) in a rotating autoclave at 350° for six hours. The reaction mixture was filtered, and benzene was removed from the filtrate at a moderately low pressure. The residue partially crystallized out at −70°, yielding 0.4 g of crystals, m.p. 76-86°. Crystallization from petroleum ether yielded 0.2 g of 2-ethyl-1-methylphenanthrene (VII), m.p. 100-102°. In admixture with a previously prepared sample of 2-ethyl-1-methylphenanthrene [1] there was no depression of melting point.

Found %: C 92.8; H 7.1
$C_{17}H_{16}$. Calculated %: C 92.7; H 7.3

The hydrocarbon was somewhat contaminated with high-melting substances, and this had an effect on the subsequent oxidation of the quinone VIII, the yield of which was low (4 mg of the quinone was obtained from 20 mg of the hydrocarbon). The quinoxaline IX, prepared from the quinone, melted at 110-111°, and showed no depression in admixture with an authentic sample [1].

Dehydrogenation of the Ketone VI

The dehydrogenation was performed as in the preceding experiment, 1.5 g of the ketone VI being used. After filtration and removal of benzene, a yellow oil remained, which did not crystallize even at −70°. It was dissolved in 10 ml of petroleum ether and chromatographed on 10 g of aluminum oxide.

Fraction I, 5 ml of petroleum ether;	213 mg, colorless oil
Fraction II, "	157 mg, yellow oil
Fraction III, "	87 mg, crystals, impregnated with oil
Fraction IV, V, each 5 ml of petroleum ether;	72 mg, crystals, impregnated with oil
Fraction VI, VII, VIII, "	58 mg, oil

Further elutions with mixtures of petroleum ether and benzene, and also with ether and with alcohol, gave only liquid fractions. Crystallization of fractions III-V from petroleum ether at − 70° yielded 23 mg of the hydrocarbon VII, m.p. 94-96°. In admixture with known 2-ethyl-1-methylphenanthrene there was no depression of melting point.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 4.9 g of the dienone II and 10.9 g of freshly distilled 2-methyl-2-cyclopenten-1-one (III) was heated in a sealed glass tube for six hours at 150°. After removal of the excess of ketone (7.0 g) under a residual pressure of 15 mm in a water bath, the residue began to crystallize out. Alcohol (3 ml) was added, and after two hours the precipitated crystals (2.0 g, m.p. 160-170°) were filtered off at the pump. The mother liquor was evaporated down, and residual methylcyclopentenone (1 g) was removed at a residual pressure of 1 mm. The residue was dissolved in a mixture of 4 ml of petroleum ether and 1 ml of benzene and was set aside for one day. A second crop of crystals (0.7 g, m.p. 160-170°) came down. The second mother liquor, after three days' standing, yielded a third crop of crystals (0.15 g, m.p. 170-180°). The total yield of a crystalline mixture of isomers of 10,14-dimethyl-9-cardosterene-2,15-dione (X A, X B, and X C) was 2.85 g (38% on the amount of dienone II taken).

By fractional crystallization from alcohol of the first and second crops of crystals, in conjunction with mechanical separation of crystals, the following isomers were obtained: X A, m.p. 184-185°, 1.45 g, and X B, m.p. 154-154.5°, 0.42 g. Crystallization of the third crop yielded the isomer X C, m.p. 192-193°, 60 mg.

Isomer X A, m.p. 184-185° (corr.).

Found %: C 79.9; 79.9; H 9.2; 9.2

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomer X B, m.p. 154-154.5°.

Found %: C 79.6; H 9.1

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Isomer X C, m.p. 192-193° (corr.).

Found %: C 79.6; 79.55; H 9.2; 9.1

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

A mixture of the isomers X A and X C melted at 160-170°.

Isomerization of the Diketone X A

A mixture of 200 mg of the diketone X A, m.p. 184-185°, 6 ml of acetic acid, 10 ml of hydrochloric acid, and 6 ml of toluene was boiled under reflux for four hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic potash, and filtered. The solvent was removed under moderately low pressure, and the crystalline residue was recrystallized from 1.5 ml of alcohol, yielding 50 mg of the original diketone X A, m.p. 182-183°. Slow evaporation of solvent from the mother liquor yielded a mixture of the diketones X A and X D, which were separated mechanically. In this way, 16 mg of 10,14-dimethyl-8-cardosterene-2,15-dione (X D) was obtained in the form of white prisms, m.p. 124-125°.

Found %: C 80.0; 79.7; H 9.0; 9.15

$C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.1

Clemmensen Reduction of the Diketone X A

A mixture of 800 mg of the diketone X A, m.p. 184-185°, 10 ml of acetic acid, 15 ml of hydrochloric acid, 6 ml of toluene, and 4 g of amalgamated zinc was boiled under reflux for 3 hours 30 minutes. The toluene layer was separated and neutralized, and the toluene was removed under reduced pressure. The residue was crystallized at − 70° from petroleum ether, yielding 50 mg of the ketone VI, m.p. 83-86°. Recrystallization from petroleum ether raised the melting point to 89-91°. A mixture melting point with the sample of VI described above gave no depression. The dinitrophenylhydrazone melted at 192-194°, and this also gave no depression in admixture with the dinitrophenylhydrazone of VI described above.

Clemmensen Reduction of the Diketone X B

The reduction was performed as in the preceding experiment: from 300 mg of the diketone X B, m.p. 154-154.5°, 20 mg of the ketone V, m.p. 49-51°, was obtained. A mixture melting point with the above-described sample of this ketone showed no depression. The dinitrophenylhydrazone melted at 191-193°, and this also gave no depression in admixture with the previous sample.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Cyclopenten-1-one (XI)

A mixture of 2.5 g of the dienone I and 5.7 g of freshly distilled 2-cyclopenten-1-one (XI) was heated in a carbon dioxide atmosphere in a sealed glass tube at 130° for 11 hours. The cyclopentenone that had not reacted (4.1 g) was distilled off at 15 mm, and the residue partially crystallized out when 5 ml of petroleum ether was added, yielding 0.4 g (11%) of a crystalline mixture of isomers (XII A and XII B) of 10-methyl-9-cardosterene-3,15-dione, m.p. 118-125°. Two recrystallizations of the mixture from petroleum ether-benzene (3 : 1) yielded 100 mg of the isomer XII A, m.p. 123-124°.

Found %: C 79.2; 79.2; H 8.9; 9.1
$C_{18}H_{24}O_2$. Calculated %: C 79.4; H 8.9

From the mother liquor, after removal of unchanged dienone I (0.5 g), 80 mg of crystals, m.p. 135-150°, were separated in the usual way. Two recrystallizations from a mixture of petroleum ether and benzene (3 : 1) yielded 20 mg of the isomer XII B, m.p. 156-157°.

Found %: C 79.4; 79.7; H 8.8; 9.0
$C_{18}H_{24}O_2$. Calculated %: C 79.4; H 8.9

Condensation of the dienone I with the cyclopentenone XI at 160° was accompanied by much resinification, and the yield of crystalline products was reduced by a factor of two.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 3,5-Dimethyl-3-cyclopentene-1,2-dione (XIII)

A solution of 1.1 g of the dienone I and 0.6 g of the diketone XIII in 3 ml of absolute benzene was heated in a carbon dioxide atmosphere in a sealed glass tube at 100° for six hours. The benzene was removed under reduced pressure, and the residue was diluted with 5 ml of ether and set aside to crystallize at −10°. After four days a considerable amount of crystals had formed, and these were recrystallized from alcohol, yielding 140 mg of the tetracyclic triketone XIV in the form of yellow needles; these show incipient melting at 108-110°, solidify again at 112-115°, and melt again at 167-168°.

Found %: C 76.1; 76.3; H 8.3; 8.5
$C_{20}H_{26}O_3$. Calculated %: C 76.4; H 8.3

The mother liquor was dissolved in petroleum ether and chromatographed on aluminum oxide. Elution with benzene yielded 100 mg of the tetracyclic diketo enol XV in the form of colorless, well-formed crystals, m.p. 167-168°. An alcoholic solution of the substance gave a violet color with an aqueous-alcoholic solution of ferric chlorides.

Found %: C 76.4; 76.6; H 8.3; 8.3
$C_{20}H_{26}O_3$. Calculated %: C 76.4; H 8.3

Isomerization of the Triketone XIV

One drop of piperidine was added to a solution of 70 mg of the triketone XIV, m.p. 108-110°, in 1.5 ml of dioxane. The solution became clear after 15 minutes' standing, and 0.5 ml of water was then added, the turbidity that appeared being removed by addition of a drop of alcohol. Colorless crystals soon began to appear, and 60 mg of the diketo enol XV, m.p. 167-168°, was obtained. A mixture melting test with the above-described sample gave no depression. When the condensation of the dienone I with the diketone XIII was carried out at 120°, it was not found possible to isolate any of the triketone XIV, only the diketo enol XV being obtained.

Condensation of 3a,4,7,7a-Tetrahydro-3,7a-dimethyl-1-indanone with Diethyl Oxalate.

3a,4,7,7a-Tetrahydro-3,7a-dimethyl-1-indanone was prepared by the condensation of 1,3-butadiene with 2,4-dimethyl-2-cyclopenten-1-one [9], and had b.p. 90-92° at 7 mm, n_D^{20} 1.4875. Ground sodium ethoxide (11 g, prepared from 3.7 g of sodium) was placed in a three-necked flask fitted with reflux condenser, and dropping funnel. The flask was filled with nitrogen, and a solution of 19.5 g of diethyl oxalate in 80 ml of benzene was added. The mixture was heated in a water bath for 10 minutes, and the sodium ethoxide went completely into solution. The solution, which had become dark in color, was cooled to 20° and was stirred while a solution of 14.6 g of 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone in 40 ml of benzene was added dropwise. Heat was evolved, and the mixture became black. It was set aside for five hours at 20°, and then treated with water. The benzene layer was neutralized by agitation with dilute hydrochloric acid, the solvent was driven off, and the residue was vacuum-distilled, yielding 11.2 g of the condensation product, b.p. 142-143° at 1 mm, n_D^{20} 1.5070.

Found %: C 68.2; 68.3; H 7.6; 7.6
$C_{15}H_{20}O_4$. Calculated %: C 68.15; H 7.6

Attempts at eliminating carbon monoxide from this product by heating with glass and iron powder at 180-200° were without result: the substance was recovered unchanged, apart from some resinification.

SUMMARY

1. Total syntheses of the steroid diketones IV and X of the cis-cis series have been effected by condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,6a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclopenten-1-one (III). From the mixtures of isomers formed (IV and X), in each case three isomeric diketones were isolated, two of which, i.e., those formed in the greatest amount, have been shown to have "inverted" structures and to differ with respect to the spatial arrangement of substituents at $C_{13}-C_{14}$.

2. 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) has been condensed also with 2-cyclopenten-1-one (XI), and two isomeric steroid diketones (XII) have been isolated.

3. Condensation of the hexahydromethylvinyl-2(1H)-naphthalenone I with 3,5-dimethyl-3-cyclopentene-1,2-dione (XIII) yielded the steroid triketone XIV, which very readily isomerizes into the diketo enol XV.

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*****See Consultants Bureau Translation, page 787.

******See Consultants Bureau Translation, page a-211.

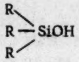
*******See Consultants Bureau Translation, page 911.

SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF ORGANOSILICON ACETALS

M. F. Shostakovsky, I. A. Shikhiev, and D. A. Kochkin

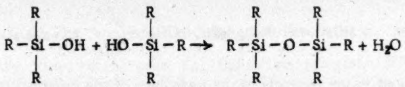
Oxygen-containing organosilicon compounds, such as silanols of general formula



$$R_3SiOH$$

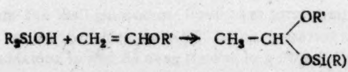
(R = alkyl or aryl), are of great theoretical interest. There are great prospects for development in organic chemistry along the line of the unification of organic and organosilicon syntheses. The authors of this paper have undertaken the task of working out new syntheses of organosilicon compounds.

It has been shown by the work of Andrianov [1] and others [2] that organosilicon compounds have certain peculiar properties. It is well known, for example, that tertiary alcohols are readily dehydrated to unsaturated hydrocarbons, whereas trialkylsilanols, on dehydration, give stable siloxane dimers:



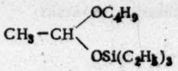
$$R_3Si-OH + HO-SiR_3 \rightarrow R_3Si-O-SiR_3 + H_2O$$

We now describe a new synthesis of oxygen-containing organosilicon compounds based on the reaction of vinyl ethers with silanols. In the course of this work we have established that the reaction of alkyl vinyl ethers with trialkylsilanols proceeds similarly to the corresponding reaction with organic tertiary alcohols and may be represented by the equation:



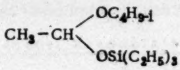
$$R_3SiOH + CH_2=CHOR' \rightarrow CH_3-CH(OR')OSi(R)_3$$

We have studied methods for the preparation of the following acetals:



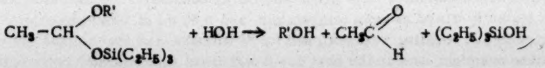
$$CH_3-CH(OC_4H_9)OSi(C_2H_5)_3$$

and



$$CH_3-CH(OC_4H_9\text{-}i)OSi(C_2H_5)_3$$

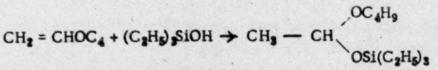
Addition of trialkylsilanols to vinyl ethers proceeds fairly readily in presence of traces of 30% hydrochloric acid, the procedure being that which has been developed for the synthesis of acetals of organic alcohols [3]. We have in this way prepared and characterized two unsymmetrical acetals: the butyl triethylsilyl and the isobutyl triethylsilyl acetals of acetaldehyde. The structures of the organosilicon acetals obtained were proved by the products of their hydrolysis, which proceeds according to the equation:



$$CH_3-CH(OR')OSi(C_2H_5)_3 + HOH \rightarrow R'OH + CH_3CHO + (C_2H_5)_3SiOH$$

EXPERIMENTAL

1. Synthesis of Acetaldehyde Butyl Triethylsilyl Acetal



$$CH_2 = CHOC_4 + (C_2H_5)_3SiOH \rightarrow CH_3 - CH\begin{matrix} OC_4H_9 \\ OSi(C_2H_5)_3 \end{matrix}$$

To a cold (room temperature) mixture of 33 g (0.25 mole) of triethylsilanol (b.p. 80°/30 mm; d_4^{20} 0.8652; n_D^{20} 1.4332) and 25 g (0.25 mole) of butyl vinyl ether (b.p. 93-94°; d_4^{20}0.7790; n_D^{20} 1.4020) 0.02 ml of 30% hydrochloric acid was added, and the temperature rose to 48°. After one hour the contents of the flask were heated under reflux in a water bath at 80-93° for one hour, and they were then set aside overnight. On the next day the reaction mixture was neutralized, and dried with potassium carbonate. The potassium carbonate was then filtered off, and the filtrate was distilled at atmospheric pressure, the following fractions being obtained:

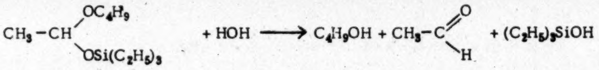
Fraction I, b.p. up to 213°; 8g
Fraction II, b.p. 214-216°; 14 g; n_D^{20} 1.4258
Fraction III, b.p. 217-218°; 22 g; n_D^{20} 1.4274
Residue 4 g

Fractions II and III were united and refractionated, yielding 32 g of a product boiling at 82-83°/ 9 mm; yield 55.17% on the amount of butyl vinyl ether taken. This substance had the following constants: d_4^{20}0.8574; n_D^{20} 1.4271; found MR 69.49; calculated for $C_{12}H_{28}SiO_2$ MR 69.85.

Found %:	C 62.49; 62.60;	Si 11.74; 11.88;	H 12.20, 12.25
$C_{12}H_{28}SiO_2$. Calculated %:	C 62.06;	Si 12.09;	H 12.07

From the results obtained it follows that the substance of b.p. 82-83°/ 9 mm was acetaldehyde butyl triethylsilyl acetal. It was a clear oily liquid having an ethereal odor; it did not change in storage.

2. Hydrolysis of the Butyl Triethylsilyl Acetal

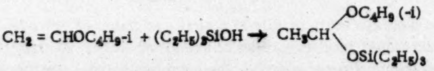


$$CH_3-CH\begin{matrix} OC_4H_9 \\ OSi(C_2H_5)_3 \end{matrix} + HOH \longrightarrow C_4H_9OH + CH_3-C\begin{matrix} =O \\ H \end{matrix} + (C_2H_5)_3SiOH$$

Acetaldehyde was estimated in the products of the hydrolysis of the unsymmetrical organosilicon acetal by the bisulfite method. It was found that hydrolysis of the acetal by treatment with 2% sulfuric acid at 60° for 12 hours did not go well, and in further work the hydrolysis was carried out in a boiling water bath in presence of 5% sulfuric acid.

The acetal (0.3213 g) was heated with 50 ml of 5% sulfuric acid in a sealed tube for six hours. The contents of the tube were then transferred to a 200-ml measuring flask and made up to volume with distilled water. Analysis by the bisulfite method gave 86.39% of acetaldehyde (of the theoretical amount). A parallel experiment by the same method (0.4391 g of acetal) gave 84.28% of acetaldehyde. Towards the end of the hydrolysis process, an oily layer formed on the surface of the solution; this was evidently one of the hydrolysis products. The hydrolysis results show that the substance of b.p. 82-83°/ 9 mm was the butyl triethylsilyl acetal. It should be noted that the described hydrolysis conditions do not yield quantitative results.

3. Synthesis of Acetaldehyde Isobutyl Triethylsilyl Acetal



$$CH_2 = CHOC_4H_9\text{-i} + (C_2H_5)_3SiOH \rightarrow CH_3CH\begin{matrix} OC_4H_9\,(\text{-i}) \\ OSi(C_2H_5)_3 \end{matrix}$$

The conditions of the synthesis were similar to those of the preceding experiment. A mixture of 33 g (0.25 mole) of triethylsilanol and 25 g (0.25 mole) of isobutyl vinyl ether (b.p. 83°; n_D^{20} 1.3986; d_4^{20} 0.7680) was placed in a 150-ml round-bottomed flask fitted with reflux condenser, thermometer, and mechanical stirrer. The mixture was constantly stirred at room temperature, and 0.02 ml of 30% hydrochloric acid was added, when the temperature rose to 45°. Stirring was continued for 90 minutes, and the temperature was raised to 84°. The mixture was set aside overnight, and on the next day it was dried with calcined potassium carbonate, and distilled, the following fractions being obtained:

Fraction I, b.p. up to 209°;	13 g
Fraction II, b.p. 210-215°;	38g
Residue	4 g

Fraction II was refractionated, and yielded 30 g (51.72% on the amount of isobutyl vinyl ether taken) of a product of b.p. 75-76°/ 7 mm.

It must be pointed out that after each distillation there remained some liquid at the bottom of the flask which was not distillable under the conditions indicated: at a higher temperature it decomposed. The constants of the product of b.p. 75-76°/ 7 mm were d_4^{20} 0.8530; n_D^{20} 1.4252; found MR 69.58; calculated for $C_{12}H_{28}SiO_2$ MR 69.85.

Found %: C 62.14; 61.97; Si 12.31; 12.10; H 12.70; 12.48
$C_{12}H_{28}SiO_2$. Calculated %: C 62.06; Si 12.09; H 12.07

From these results it will be seen that the product of b.p. 75-76°/ 7 mm was acetaldehyde isobutyl triethylsilyl acetal. It was a clear oily liquid having an ethereal odor.

In conclusion it must be pointed out that organosilicon acetals are comparatively stable substances. The butyl triethylsilyl acetal is evidently more stable than the isobutyl compound.

SUMMARY

1. It has been shown, for the first time, that triethylsilanol condenses with butyl vinyl and isobutyl vinyl ethers under conditions similar to those required in the corresponding syntheses with organic alcohols.

2. Two unsymmetrical organosilicon acetals of acetaldehyde, the butyl triethylsilyl and isobutyl triethylsilyl acetals, have been synthesized and described for the first time.

3. The proposed method is a general one for the preparation of various organosilicon acetals from alkyl vinyl ethers and trialkylsilanols.

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EFFECT OF COMPRESSION ON THE POROSITY, CATALYTIC PROPERTIES, AND CHROMATOGRAPHIC ACTIVITY OF SILICA GEL

L. Kh. Freidlin, L. F. Vereshchagin, I. E. Neimark,
I. U. Numanov, and R. Yu. Sheinfain

As we have previously shown [1, 2], the porosity characteristics of silica gel greatly influence its activity and selectivity in the vapor-phase hydrolysis of chlorobenzene. When in addition to a large volume of fine pores the silica gel has a sufficiently large volume of connective pores through which the reactants and products can be transported to active centers, it forms a catalyst upon which diffusional retardation is not observed. When, on the contrary, the volume of connective pores is insufficiently large and the internal surface is not readily accessible, diffusional retardation of the process is to be observed. It is natural to suppose that, if we apply a high pressure to the silica gel, its specific surface and porosity characteristics will alter, and, at the same time, its adsorption and catalytic properties will also alter.

EXPERIMENTAL

Variation in the Porosity Characteristics of Silica Gels Compressed at Various Pressures.

The samples of silica gels were compressed in copper ampoules, 50 mm in length, 10 mm in external diameter, and 9.6 mm in internal diameter. In order to distribute the pressure evenly over the whole of the ampoule, the latter was wrapped in lead foil. Finely ground silica gel was rammed tightly into the ampoule, which was then closed and subjected to pressure in the multiplier described previously [3].

Structural Characteristics of Samples of Silica Gel Before and After Compression at Various Pressures

Figures 1 and 2 show the sorption isotherms for methanol vapor on silica gel, before and after compression. It will be seen from Table 1 that the reduction in the limiting sorptive capacity of the pores resulting from an increase in compression from zero to 5000 atm was considerably greater for the sample having the larger pores. For this sample the further reduction in sorptive capacity due to increase in compression from 5000 to 10,000 atm was much less, and there was practically no further reduction when the compression was increased to 20,000 atm. The greatest reduction for the coarse sample occurred, therefore, in the 0-5000 atm range, whereas it will be seen that, for finely porous silica gel, the greatest reduction occurred in the 5000-10,000 atm range. Reduction of the limiting sorptive capacity of the pores by means of compression was therefore effected more readily for the coarser silica gel, which had the greatest volume of connective pores. Although the limiting sorptive capacity of the pores of the coarsely porous sample was greatly reduced by increase in compression from zero to 5000 atm, there was no corresponding change in specific surface; whereas, in the 10,000-20,000 atm range, in which there was only a small fall in the limiting sorptive capacity, there was an appreciable reduction in specific surface. Mechanical action, therefore, leads mainly to the destruction of connective pores, whereas thermal action leads mainly to the destruction of the fine pores [2].

Table 1 shows also that, although the limiting sorptive capacity of the pores of the coarsely porous sample was 0.80 ml/g, and that of the finely porous silica gel only 0.34 ml/g, compression at 10,000 atm resulted in a leveling out of the limiting sorptive capacities of the two samples, which were reduced to 0.19-0.21 ml/g and were not appreciably reduced further when the pressure was raised to 20,000 atm. The limit of compression of the silica gel was evidently already attained at 10,000 atm The sorption isotherm for silica gel compressed at 5000 atm shows considerable hysteresis, i.e. a part of the connective pores were preserved (Fig. 2, Curve 1). On the other hand, the sorption isotherms for the samples compressed at 10,000 and 20,000 atm show very little hysteresis and are almost coincident (Figs. 1 and 2, Curve 2). At such pressures, therefore, the connective pores were almost completely destroyed.

TABLE 1

Structural Characteristics of Eight Samples of Silica Gel (Not Compressed, and Compressed at Various Pressures)

Sample of silica gel	Coarsely porous				Finely porous			
	not compressed	compressed at			not compressed	compressed at		
		5000 atm	10000 atm	20000 atm		5000 atm	10000 atm	20000 atm
Limiting sorptive capacity of the pores (sum of volumes of micro and connective pores) (ml/g)	0.80	0.38	0.21	0.19	0.34	0.29	0.19	0.19
Specific surface (sq.m/g)	350	350	310	260	680	–	290	290

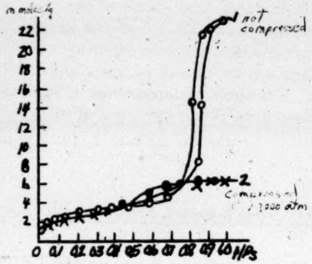

Fig. 1. Adsorption isotherms for methanol vapor on coarsely porous silica gel: 1) not compressed; 2) compressed at 10,000 atm.

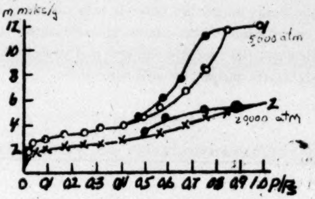

Fig. 2. Adsorption isotherms for methanol vapor on coarsely porous silica gel: 1) compressed at 5000 atm; 2) compressed at 20,000 atm

Conditions of the Catalytic Experiments, and the Analytical Method

The reaction was carried out in a continuous-flow system. Water and chlorobenzene were supplied from two automatically regulated burets [4], and passed to a quartz flask at 250°, which served as a superheater, and then from the side tube of the flask to the reaction tube containing the catalyst. The water-chlorobenzene ratio was close to unity in all experiments. The volume of catalyst was 10 ml. Each experiment lasted 90 minutes, and in the course of this time 4 ml of chlorobenzene and 5 ml of water were passed. All the silica gel samples were promoted by cupric chloride (2%). Regeneration of the catalyst was effected by a two-hour treatment with air at 500°, following experiments at 500, 550, and 600°. The reaction products were analyzed for phenol and hydrochloric acid.

Comparative Activity, Productivity, and Specificity of Samples of Silica Gel Compressed at Various Pressures

It will be seen from Figures 3 and 4 that the activity per unit volume, i.e. the productivity, of coarsely porous silica gel depends on the reaction temperature and on the pressure at which the silica gel was compressed. The productivity of the sample compressed at 5000 atm was higher than that of the uncompressed sample at all temperatures from 400° to 550°. The productivity of the sample compressed at 10,000 atm was about equal

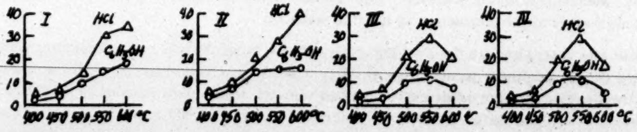

Fig. 3. Hydrolysis of chlorobenzene in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures): I) not compressed; II) compressed at 5000 atm; III) compressed at 10,000 atm; IV) compressed at 20,000 atm

to, and the one compressed at 20,000 atm somewhat lower than, the original uncompressed sample. The specific volume of the silica gel was reduced by a factor of about 1.5 by compression at 20,000 atm, so that its specific activity (i.e., activity per unit weight) was lower than that of the uncompressed material.

For the finely porous silica gel, the rise in productivity due to compression at 500 atm was less, and the fall in specific activity was still greater than before (Figs. 5 and 6). The effect of compression at 20,000 atm was particularly great for the finely porous silica gel S-1. Not only the specific activity, but also the productivity, of this catalyst was lower after compression (Table 2.).

The selectivity of samples compressed at 5000 atm was very little different from that of the uncompressed samples, and the selectivity of samples compressed at 10,000 and 20,000 atm was lower than that of the uncompressed sample (Figs. 7 and 8). The greater the compression employed, the lower the temperature at which side processes made their appearance. The higher the temperature, the greater the importance assumed by the side processes on the compressed samples of silica gel and the higher the yield of acid as compared with that of phenol.

The results are completely in agreement with the changes in density and porosity characteristics occurring during compression. On the one hand, increase in pressure results in an increase in the density of the sample, and for this reason the productivity of a sample compressed at 5000 atm is greater than that of the original sample. On the other hand, the higher the pressure under which the silica gel is compressed, the more inaccessible does its active surface become, the more rapidly does it become carbonized, and the more prominent do the side processes become. For this reason, the productivity of a sample compressed at 20,000 atm is less than that of the uncompressed sample.

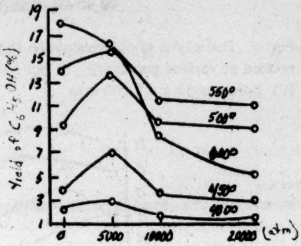

Fig. 4. Yield of phenol in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures).

TABLE 2
Productivity and Specificity of Uncompressed and Compressed Samples of Silica Gel S-1

Not compressed				Compressed			
Temperature (°C)	Yield (%)		$\frac{HCl}{C_6H_5OH}$	Temperature (°C)	Yield (%)		$\frac{HCl}{C_6H_5OH}$
	C_6H_5OH	HCl			C_6H_5OH	HCl	
450	7.3	8.1	1.1	400	2.9	4.0	1.4
500	15.7	16.2	1.0	450	6.2	8.9	1.5
550	29.1	31.4	1.1	500	8.4	11.6	1.4
600	36.6	42.9	1.1	550	16.1	21.9	1.4
650	38.4	53.0	1.4	600	21.0	31.8	1.5

Effect of Compression on the Chromatographic Activity of Silica Gel

Ground silica gel was fractionated by passage through sieves, and the 100/200 mesh per sq. in. fraction was separated and dried at 150° for 5-6 hours. The silica gel prepared in this way was rammed tightly into a glass tube, diameter 10 mm and length 500 mm, which was fitted with a jacket (thermostat). A mixture of benzene (10% by volume) and heptane (90% by volume) of refractive index n_D^{20} 1.3980 was prepared, and 20 ml of it was passed through the silica gel column at a rate of about 0.8 ml per minute. The liquid passing through was collected in a receiver, and it was tested periodically for benzene by the formolite reaction. An orange coloration indicated that benzene was beginning to pass and the sorbent was completely saturated.

The chromatographic activity a (ml/g) was calculated by the formula $a = \frac{b \cdot c \cdot 100}{m \cdot d}$, where b is the benzene content (% by vol.) of the original mixture; c is the amount (ml) of pure heptane separated in the chromatographic process; d is the heptane content (% by vol.) of the original mixture; and m is the weight (g) of silica gel [5].

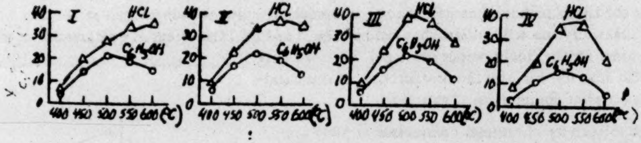

Fig. 5. Hydrolysis of chlorobenzene in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures): I) not compressed; II) compressed at 5000 atm; III) compressed at 10,000 atm; IV) compressed at 20,000 atm

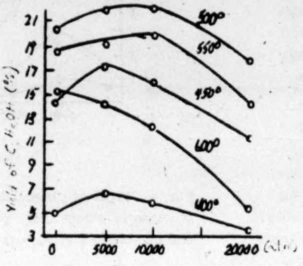

Fig. 6. Yield of phenol in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures)

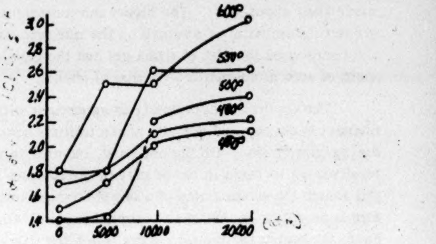

Fig. 7. The ratio of the yields of HCl and C_6H_5OH in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures)

TABLE 3

Chromatographic Activity of the Original Silica Gel (10 g)

Time (min.)	Temp. of water jacket (°C)	Vol. of pure heptane obtained (ml)	Rate of efflux of heptane (drops/sec)	No. of drops of liquid until positive test with formaldehyde obtained
3	+2	1.0	3.4	−2
11	+2	3.0	4.0	−1
19	+2	5.0	4.0	−1
29	+2	7.0	4.0	−2
39	+2	8.4	4.0	+2
Total 39	Mean +2	Total 8.7	Mean 4.0	Total 6

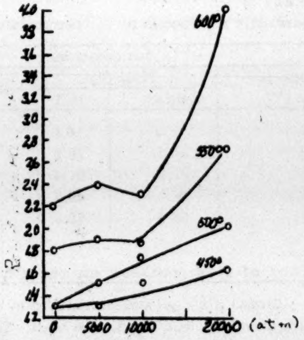

Fig. 8. The ratio of the yields of HCl and C_6H_5OH in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures).

Six drops, i.e., 0.3 ml of liquid, were tested before a positive reaction with formaldehyde were obtained. Altogether, therefore, 8.7 ml of pure heptane was separated chromatographically: the chromatographic activity of the uncompressed sample of silica gel was 9.7 ml/g (Tables 3 and 4). The chromatographic activity of silica gel compressed at 20,000 atm was 7.3 ml/g, i.e., was about 25% less than its activity in the uncompressed state. No doubt the explanation of this behavior is that the compression process alters the porosity characteristics and specific surface of the silica gel.

TABLE 4
Chromatographic Activity of Silica Gel Compressed at 20,000 atm (11.7 g)

Time (min.)	Temp. of water jacket (°C)	Vol. of pure heptane obtained (ml)	Rate of efflux of heptane (drops/sec)	No. of drops of liquid until positive test with formaldehyde obtained
10	+ 2	2.0	4.0	−2
20	+ 2	4.0	4.0	−2
30	+ 2	6.0	4.0	−2
36	+ 2	7.1	4.0	+2
Total 36	Mean + 2	Total 7.4	Mean 4.0	Total 6

SUMMARY

1. An investigation has been made of the effect of pressures of up to 20,000 atm on the porosity characteristics, adsorption activity, and catalytic properties of silica gel.

2. It has been shown that the greatest reduction (by 50%) in the limiting sorptive capacity of the pores (sum of the capacities of the micro and connective pores of the coarsely porous silica gel) occurs during compression to 5000 atm, but no simultaneous change in specific surface occurs. The greatest reduction in the limiting sorptive capacity of the pores of the finely porous silica gel occurs over the range 5000-10,000 atm. The reduction in the limiting sorptive capacity of the pores is therefore attained by a lower compression for the coarsely porous silica gel. The explanation of this is that the coarsely porous silica gel, unlike the finely porous material, has a greater volume of connective pores. Mechanical action, therefore, primarily destroys the connective pores, whereas thermal action destroys the fine pores. In general, the limiting sorptive capacity of the coarsely porous silica gel compressed at 5000-10,000 atm does not differ from that of the finely porous material, i.e., the coarsely porous material is converted by pressure into finely porous material. When the compression is further increased to 20,000 atm, the limiting sorptive capacity of the pores of the samples of finely and coarsely porous silica gels remains practically the same as that of the samples compressed at 10,000 atm.

3. Compression at 20,000 atm results in reduction of the specific surface of coarsely porous silica gel from 350 to 260 sq.m/g, and that of the finely porous silica gel from 680 to 290 sq.m/g, i.e., by 26% and 57%, respectively.

4. The productivity of samples compressed at 5000 atm is higher, and of those compressed at 20,000 atm lower, than that of the uncompressed sample. The greater the compression, the lower the specific activity.

5. The selectivity of samples compressed at 5000 atm differs little from that of the uncompressed sample, but samples compressed at higher pressures have greatly reduced selectivity. It is possible that samples that have been subjected to higher compression, i.e., have a more severely destroyed porous structure, more readily sinter together, and so become deactivated.

6. It has been shown that the chromatographic activity of silica gel compressed at 20,000 atm is about 25% less than that of the uncompressed sample.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 62 [1]. POLYCONDENSATION OF ACID ESTERS OF ADIPIC ACID WITH VARIOUS GLYCOLS

V. V. Korshak and S. V. Vinogradova

In an investigation of the polycondensation of 1,6-hexanediol with sebacic acid [2], we have shown that at the beginning of the reaction a low-molecular-weight polyester (molecular weight of up to 800) is formed, and that this is further converted into a macromolecular polyester, and is therefore the starting material for the building up of the latter. The low-molecular-weight polyester is probably a mixture of the following compounds: $HO(CH_2)_6OOC(CH_2)_8COOH$; $HOOC(CH_2)_8COO(CH_2)_6OOC(CH_2)_8COOH$; $HO(CH_2)_6OOC(CH_2)_8COO(CH_2)_6OH$; $H[O(CH_2)_6OOC(CH_2)_8CO]_2OH$; and so on, right up to the trimer $H[O(CH_2)_6OOC(CH_2)_8CO]_3OH$.

In order to gain an understanding of the mechanisms of the elementary reactions and of their roles in the polyesterification process, it was necessary to study the reactions of these individual substances and their interaction with one another. With this object we investigated the behavior under polycondensation conditions of neutral esters of glycols with dicarboxylic acids, the example taken being bis(2-hydroxyethyl) sebacate, and we found that they were able to give polyesters under these conditions [3]. No less interest is presented by a study of the behavior of acid esters of glycols with dicarboxylic acids (of the type $HOOCRCOOR^1OOCRCOOH$), for such esters are possible intermediate products in the first stages of the polyesterification process, and a knowledge of the further transformations that they may undergo is very essential for an understanding of the process as a whole.

We have therefore synthesized two acid esters of adipic acid with glycols: an ester formed by adipic acid with ethylene glycol $HOOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4COOH$, and an ester formed by adipic acid with 1,20-eicosanediol $HOOC(CH_2)_4COO(CH_2)_{20}OOC(CH_2)_4COOH$. They were prepared by heating adipic acid (10 parts) with the glycol (1 part) in presence of a small amount of camphorsulfonic acid. The reaction product was extracted with benzene, and then precipitated with petroleum ether. The acid diadipic ester of ethylene glycol was a white substance, m.p. 80°, and the diadipic ester of eicosanediol was a white substance, m.p. 83°. The ethylene glycol ester was subjected to a polycondensation treatment under the usual conditions [4] in condensation tubes at 200° at a residual pressure of 1-2 mm Hg. The results obtained are shown in the table.

TABLE

Duration of heating (hr.)	Sp. viscosity of a 0.5% soln. of the ethylene glycol ester in benzene	Viscosimetric mol. wt.
1	0.034	1257
2	0.034	1257
3	0.035	1294
6	0.039	1440
9	0.039	1440

There can be no doubt, therefore, that this acid diadipic ester of ethylene glycol is able to undergo polycondensation with formation of a low-molecular-weight polyester. The acid diadipic ester of 1,20-eicosanediol, heated for 11 hours under the same conditions, formed a polyester of molecular weight 1420, i.e., no essential difference between the behavior of the two esters was to be observed. This can be readily understood, for the polycondensation of acid esters of glycols must proceed as an acidolysis reaction, being an example of transesterification, and must lead in both cases to the elimination of the same substance, adipic acid, according to the equation:

$$xHOOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4COOH \rightarrow (x-1)HOOC(CH_2)_4COOH +$$

$$+ HOOC(CH_2)_4CO[O(CH_2)_2OOC(CH_2)_4CO]_xOH$$

In this case the elementary reaction is one of acidolysis, i.e., the splitting of an ester link under the action of an acid carboxyl group, accompanied by transfer of an acid hydroxyl from one acid residue to another, as shown in the following equation, which represents the first stage of the interaction of two molecules of the acid adipic ester of ethylene glycol:

$$\mathrm{HOOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4CO\,\vdots\,OH + HOOC(CH_2)_4CO\,\vdots\,O(CH_2)_2OOC(CH_2)_4COOH} \rightarrow$$

$$\rightarrow \mathrm{HOOC(CH_2)_4COOH + HOOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4COOH}$$

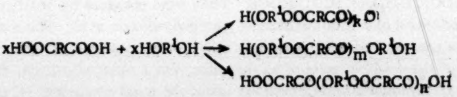
It is of interest to note that the occurrence of polycondensation with elimination of adipic acid was long ago declared to be highly likely by one of us with Golubev [5], and the present investigation has fully confirmed this statement, having shown experimentally the possibility of the polycondensation of acid esters of glycols and the formation of polyesters with elimination of a dicarboxylic acid.

When the polycondensation of acid dicarboxylic esters of glycols is compared with that of neutral esters, the high rate of the reaction in the second case, with formation of polyesters of higher molecular weight, becomes obvious. This difference must, of course, be related to the volatility of the substance eliminated during the reaction. As the volatility of adipic acid is comparatively low, both the rate of polycondensation of the acid adipic ester of the glycol and the molecular weight of the polyester formed must be low.

The results of the investigation of the elementary reactions of the polyesterification process lead us to conclude that this process is much more complex than was thought. It is necessary to assume that the growth of the chain of the polyester macromolecule proceeds as a result of reactions of three types: 1) direct esterification reactions between terminal hydroxyl and carboxyl groups of the starting substances and those of the growing macromolecule; 2) transesterification reactions of glycol esters formed at various stages of the process and reacting with one another via alcoholysis reactions; and 3) transesterification reactions of acid dicarboxylic esters formed at various stages of the process and reacting with one another via acidolysis reactions. The parts played by the first two reactions are evidently nearly the same, and this may explain the long known fact that an excess of glycol is very advantageous in the polyesterification reaction [6]. The third reaction, esterolysis, must have a less important role than the first two, but it cannot be disregarded entirely, since under certain conditions its significance may become very high. In order to illustrate these statements we present below a scheme of reactions that occur in the polyesterification process and determine to some extent or other the growth of the polyester macromolecule.

Scheme of Synthetic Reactions in the Polyesterification Process

Stage 1. Reaction of the starting substances with formation of three types of products, differing in the nature of their terminal groups:



$$\mathrm{xHOOCRCOOH + xHOR^1OH} \rightarrow \begin{cases} \mathrm{H(OR^1OOCRCO)_k OH} \\ \mathrm{H(OR^1OOCRCO)_m OR^1OH} \\ \mathrm{HOOCRCO(OR^1OOCRCO)_n OH} \end{cases}$$

where k, m, or n may be 1, 2, or 3.

Stage 2. Reaction with one another of the low-molecular-weight polyesters formed in the first stage by the direct esterification mechanism (a), the alcoholysis mechanism (b), and the acidolysis mechanism (c):

a) 1. $\mathrm{H(OR^1OOCRCO)_kOH + H(OR^1OOCRCO)_kOH \rightarrow H(OR^1OOCRCO)_{2k}OH + H_2O}$

2. $\mathrm{H(OR^1OOCRCO)_mOR^1OH + HOOCRCO(OR^1OOCRCO)_nOH \rightarrow H_2O +}$

$\mathrm{+ H(OR^1OOCRCO)_{m+n+1}OH}$

3. $\mathrm{H(OR^1OOCRCO)_k OH + H(OR^1OOCRCO)_mOR^1OH \rightarrow H_2O + H(OR^1OOCRCO)_{k+m}OR^1OH}$

4. $\mathrm{HOOCRCO(OR^1OOCRCO)_nOH + H(OR^1OOCRCO)_kOH \rightarrow H_2O +}$

$\mathrm{+ HOOCRCO(OR^1OOCRCO)_{m+n}OH}$

b) 1. $\mathrm{HO(OCRCOOR^1O)_kH + H(OR^1OOCRCO)_kOH \rightarrow HOR^1OH + HOOCRCO(OR^1OOCRCO)_{2k-1}OH}$

2. $\mathrm{H(OR^1OOCRCO)_mOR^1OH + H(OR^1OOCRCO)_mOR^1OH \rightarrow HOR^1OH + H(OR^1OOCRCO)_{2m}OR^1OH}$

3. $\mathrm{H(OR^1OOCRCO)_mOR^1OH + H(OR^1OOCRCO)_kOH \rightarrow HOR^1OH + H(OR^1OOCRCO)_{k+m}OH}$

c) 1. $\mathrm{H(OR^1OOCRCO)_kOH + HO(OCRCOOR^1O)_kH \rightarrow HOOCRCOOH + H(OR^1OOCRCO)_{2k-1}OR^1OH}$

2. $\mathrm{HOOCRCO(OR^1OOCRCO)_nOH + HOOCRCO(OR^1OOCRCO)_nOH \rightarrow HOOCRCO(OR^1OOC\,RCO)_{2n}OH}$

$\mathrm{+ HOOCRCOOH}$

In this scheme we have purposely omitted destructive reactions of hydrolysis, acidolysis, alcoholysis, etc., which, as has been shown by one of us in conjunction with Zamyatine [7], Rafikov [8], Golubev [9], Kolesnikov [10], Vinogradova [11], and Chelnokova [12], play an enormous part in the polycondensation process, determining the molecular weight and molecular weight distribution function of the polymers obtained: the corresponding schemes have been published already and have been discussed in detail. We here concentrate our attention on synthetic reactions, which were previously thought to be relatively simple, but have now been found, as a result of this investigation, to be very complex.

In conclusion, attention must be drawn to the fact that alcoholysis and acidolysis reactions, which were previously regarded only as destructive processes leading to a reduction in the molecular weight of the polymer, must now be included also among the synthetic processes that lead to an increase in the molecular weight of the polymer. The part played by either of these chemical processes (whether it will be synthetic or destructive) depends not on its chemical nature, but on how readily the product of the process can be removed from the sphere of reaction. If this product is readily removed, the process will be synthetic; otherwise, a destructive process will occur.

EXPERIMENTAL

Acid Diadipic Ester of Ethylene Glycol. Adipic acid (354 g) and ethylene glycol (15 g) were placed in a flask, a few crystals of camphorsulfonic acid were added, and the mixture was heated in a bath of Wood's metal. Heating was continued for ten hours, the temperature being maintained in the range 160-170°, so that the reaction mixture formed a homogenous melt. The molten mass was poured into a mortar and, when cool, was ground to a fine powder, which was placed in a round-bottomed flask fitted with reflux condenser and then extracted with dry benzene. The benzene solution was separated from the excess of adipic acid and filtered, and addition to the cooled benzene solution of an equal volume of petroleum ether resulted in the precipitation of the acid diadipic ester of ethylene glycol, which was dried in the air, yielding 47 g (61%) of white powder, m.p. 80°.

Found %: C 52.87; 52.66; H 6.98; 6.98
$C_{14}H_{22}O_8$. Calculated %: C 52.83; H 6.91

The acid number was 343; the formula $C_{12}H_{20}O_4(COOH)_2$ requires 351.

Acid Diadipic Ester of 1,20-Eicosanediol. 1,20-Eicosanediol (15.5 g) was heated with adipic acid (69.6 g) in presence of a small amount of camphorsulfonic acid for ten hours at 170°, and the further treatment and purification was carried out as in the first experiment. A yield of 12 g (44.2%) of the acid diadipic ester of 1,20-eicosanediol was obtained as a white powder, m.p. 83°.

Found %: C 66.83; 66.81; H 10.12; 10.12
$C_{32}H_{58}O_8$. Calculated %: C 67.39; H 10.17

The acid number was 203; the formula $C_{30}H_{56}O_4(COOH)_2$ requires 196.

SUMMARY

1. A study has been made of the polycondensation of acid adipic esters of glycols, namely, the acid diadipic esters of ethylene glycol and of 1,20-eicosanediol.

2. It has been shown that acid esters of glycols are able to undergo polycondensation and form polyesters.

3. It has been shown that in the polyesterification process the growth of the polyester chain occurs not only on account of reaction between terminal groups (direct esterification), but also on account of transesterification processes (alcoholysis and acidolysis).

4. A scheme has been proposed for the synthetic reactions occurring in the polyesterification process.

5. Acid esters of adipic acid – diadipic esters of ethylene glycol and of 1,20-eicosanediol – have been prepared.

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ADSORPTION OF GAS MIXTURES

COMMUNICATION 4. ADSORPTION OF WATER AND ETHYL CHLORIDE VAPORS ON ACTIVE CHARCOAL

B. P. Bering and V. V. Serpinsky

INTRODUCTION

Investigation of the simultaneous adsorption of the vapors of water and of an organic substance on active charcoal presents considerable interest in connection with the unusual character of the adsorption isotherms for water vapor on this adsorbent. As is well known, it has been established as the result of numerous investigations on the adsorption of water vapor on charcoal, carbon black, and graphite that for all these chemically similar adsorbents the adsorption isotherms of water vapor differ greatly in form from those of organic vapors. These facts clearly point to an essential difference in the mechanism of adsorption in the two cases. There is reason to suppose that investigation of the simultaneous adsorption of aqueous and organic vapors on charcoal will enable certain supplementary information to be obtained which is necessary for the elucidation of the nature of the adsorption of water on adsorbents of the active-charcoal type.

These considerations prompted us to make a study of the simultaneous adsorption of water and an organic substance on active charcoal, and for the second component of the gas phase we chose ethyl chloride. In the study of this system we found that it was not possible to make use of the method of measuring adsorption from gas mixtures that we developed and used for the investigation of simultaneous adsorption from the mixtures $CO_2 + C_2H_4$ and $C_2H_4 + C_3H_8$ onto active charcoal [1-3]: it was found that the readings of the gas analyzer were unstable in an atmosphere of ethyl chloride. We, therefore, had to develop a new method of measurement. This new method of measuring simultaneous adsorption from binary gas mixtures, which we have called the "volumetric-gravimetric" method [4], enabled us to carry out the projected investigations. In view of its simplicity and fairly high degree of universality, we shall examine this method in greater detail.

Volumetric-Gravimetric Method

In principle, the volumetric-gravimetric method of measuring simultaneous adsorption from gas or vapor mixtures is as follows. Known amounts of the two components of the gas phase, measured with the aid of gas buret and manometer, are introduced into a vessel of known volume containing the adsorbent, which has been weighed on an adsorption balance. By measuring the total adsorption with the help of the balance and the equilibrium pressure of the gas phase with a manometer, we may determine the adsorption of each component separately and its partial pressure in the gas phase.

Thus, let $\underline{G}$ be the weight of adsorbent determined on a quartz balance suspended in the vessel, which is of volume $\underline{V}$. Let $\underline{m}$ be the total adsorption of the two components, $\underline{P}$ the equilibrium pressure of the gas phase, and n_1^0 and n_2^0 the amounts (in moles) of the two components introduced into the vessel; then, treating the gas phase as ideal, we may write the following obvious relationships:

$$m_1 + m_2 = m; \tag{1}$$

$$m_1/M_1 + m_2/M_2 = n_1^0 + n_2^0 - PV/RT = n, \tag{2}$$

(m_1 and m_2 are the values of the adsorption for the two substances [in grams]; M_1 and M_2 are the molecular weights of the components; and $\underline{n}$ is the total number of moles of the two substances in the adsorption phase).

These equations may be solved for m_1 and m_2 to give the adsorption values for the two components:

$$m_1 = \frac{n - m/M_2}{\frac{1}{M_1} - \frac{1}{M_2}}\ ; \quad m_2 = \frac{n - m/M_1}{\frac{1}{M_2} - \frac{1}{M_1}}\ . \tag{3}$$

from which we can readily determine the numbers of moles of the two components in the adsorption phase $n_1 = m_1/M_1$ and $n_2 = m_2/M_2$; the corresponding adsorption values for the two components (per gram of adsorbent),

$a_1 = n_1/G$ and $a_2 = n_2/G$; and the number of moles in the gas phase, $n'_1 = n_1^0 - n_1$ and $n'_2 = n_2^0 - n_2$, and so the partial pressures p_1 and p_2 of the two components:

$$p_1 = \frac{n'_1}{n'_1 + n'_2}P; \quad p_2 = \frac{n'_2}{n'_1 + n'_2}P. \tag{4}$$

EXPERIMENTAL

A diagram of the apparatus for measuring the adsorption of the mixture by the volumetric-gravimetric method is given in Figure 1. The sample of active charcoal ($\underline{G}$ = 0.175 g) was placed in the pan $\underline{A}$ of the quartz sorption balance $\underline{B}$, which was suspended from a hook on an internal dry joint $\underline{J}$ in the vessel $\underline{C}$. The balance was mounted on a glass frame provided with a scale for the readings, which could be made with a constant absolute accuracy over a wide range of spring extension [5]. The position of the pointer could be read within ± 2 divisions of the ocular micrometer of a cathetometer, which corresponds to an absolute displacement of the pointer of ± 0.004 mm. The balance was previously calibrated at the working temperature (74°) of the thermostat in which it was used: it had a sensitivity of 8.58×10^{-6} g per division of the ocular micrometer.

The glass piston pump $\underline{H}$ was incorporated in the apparatus in order to circulate the gas mixture through the vessel containing the balance and so accelerate attainment of adsorption equilibrium. The gas buret $\underline{G}$, which was connected to the manometer M_1, served for the measurement of portions of the two components of the gas mixture. Through the mercury cut-off S_2, which was provided with two ground glass valves, the buret could be connected to one of two reservoirs (not shown in the diagram), containing water and ethyl chloride respectively. Measurements of the pressure of the vapor in the buret and of the equilibrium pressure in the vessel $\underline{C}$ were performed with two identical manometers M_2 and M_1, the readings being accurate within ± 0.05 mm. A detailed description of the pump $\underline{H}$ and the manometers has been given in one of our papers [1].

In order to increase the accuracy of pressure measurements on water vapor, it was decided to carry out all measurements at an elevated temperature. For this purpose the adsorbent was placed during the experiment in the thermostat T_1, which was fed through a coil with water from an ultrathermostat. With the help of this thermostat the temperature of the adsorbent was maintained at 74 ± 0.01°. The whole apparatus was placed in the air thermostat T_2 (shown in Figure 1 by the broken line), in which a somewhat lower temperature (72 ± 0.5°) was maintained in order to prevent the possible condensation of mercury vapor on the adsorbent.

Before the simultaneous-adsorption measurements were carried out, preliminary experiments were performed on ethyl chloride alone and on water vapor alone, in order to check the calibration of the balance and of the volume $\underline{V}$. The adsorption values calculated from the volumetric measurements were in good agreement with those obtained by direct measurement with the balance. First of all the adsorption isotherms were determined for H_2O and C_2H_5Cl, and then four series of measurements were made on simultaneous adsorption from H_2O / C_2H_5Cl mixtures. Before each series of experiments, the adsorbent was degassed for two hours at 420° to a vacuum of about 1×10^{-4} mm Hg.

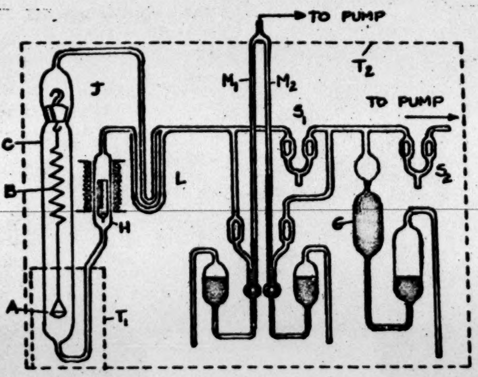

Figure 1. Diagram of apparatus

The substances taken for adsorption were distilled water and a very pure medicinal preparation of ethyl chloride. Both substances were carefully freed from dissolved gases and were contained in reservoirs that were isolated by mercury cut-offs from the remainder of the apparatus.

In the series of experiments on the adsorption of mixtures, a certain amount of C_2H_5Cl was introduced into the buret through the cut-off S_2, S_1 being closed; and after being measured it was transferred quantitatively to the vessel C by cooling the trap L with liquid nitrogen. The change in weight of the adsorbent and the equilibrium pressure were then measured, and after that a portion of water vapor was introduced into the buret. The measured portion of water was transferred through the cut-off S_1 to the vessel C by cooling the trap with liquid nitrogen. In the course of this operation, the greater part of the ethyl chloride adsorbed on the charcoal was desorbed and transferred to the trap. The cut-off S_1 was then closed, the trap L was warmed, the pump H was switched on, and observations were made on the position of the balance and the readings of the manometer M_1. When equilibrium had been established and the equilibrium values of the adsorption and pressure had been measured, the next portion of water was measured in the buret and transferred to the vessel C. In this way, in every series of measurements the total amount of C_2H_5Cl in the gas phase and on the adsorbent remained constant. In this method of measurement, when the trap L warmed up after removal of the Dewar vessel containing liquid nitrogen, first of all the ethyl chloride evaporated and was the first to be adsorbed by the charcoal, and then water evaporated from the trap and the slow process of adsorption of water set in.

Results

With the aid of the method described, measurements were made of the adsorption isotherms of the pure components, H_2O and C_2H_5Cl on active charcoal at 74° over a range of relative pressures p/p_s of 0 to 0.85 (i.e., from 0 to 240 mm Hg) for water and over the range 0 to 500 mm Hg for ethyl chloride; also, four series of adsorption measurements were made on H_2O/C_2H_5Cl mixtures at the same temperature. Since the adsorption of each component of the mixture is a function of two independent variables (the equilibrium partial pressures p_1 and p_2 of the two components), we have

$$a_1 = f_1(p_1, p_2); \quad a_2 = f_2(p_1, p_2). \tag{5}$$

Here, as in the further discussion, the subscript 1 refers to water and the subscript 2 to ethyl chloride.

Figure 2 shows the projection of the experimental points (in coordinates p_2 and p_1) on the coordinate plane $a_1 = 0$. The four curves 1, 2, 3, and 4 drawn through these points correspond to the four series of experiments. Each curve refers to a constant amount n_2^0 of ethyl chloride in the system: for curves 1, 2, 3, and 4 the values of n_2^0 are 0.112, 0.552, 1.332, and 3.091 millimoles of C_2H_5Cl respectively.

In Figure 3 the curve A is the adsorption isotherm for water vapor in absence of ethyl chloride, and curves 1–4 represent projections on the coordinate plane $p_2 = 0$ of the water-vapor adsorption isotherms corresponding to curves 1 – 4 in Figure 2. In Figure 4 curves 1–4 are projections on the same coordinate plane $p_2 = 0$ of the C_2H_5Cl adsorption isotherms corresponding to curves 1–4 in Figure 2. In both cases projections of the experimental points are marked by circles.

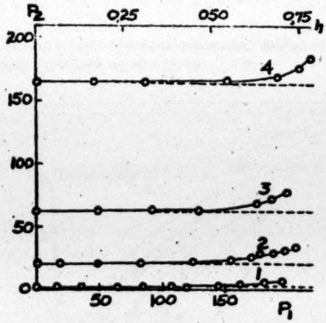

Figure 2. Projection of experimental points on the plane $a_1 = 0$.

On the scale chosen the curves in Figures 3 and 4 are practically indistinguishable from those referring not to a constant content of C_2H_5Cl in the system, but to a constant partial pressure p_2 over the adsorbent, i.e., are practically indistinguishable from the curves obtained by taking sections with the planes p_2 = constant of the isothermal adsorption surfaces for H_2O and C_2H_5Cl; these planes are indicated on Figure 2 by the broken lines. On this account we shall consider, for simplicity, that the curves in Figures 3 and 4 correspond to constant values of p_2, equal to 2, 20, 62, and 164 mm Hg for curves 1, 2, 3, and 4, respectively.

Discussion of Results

As will be seen from Figure 3, the presence of ethyl chloride in the gas phase greatly alters the character of the adsorption of water on charcoal. As the partial pressure of C_2H_5Cl increases, the water adsorption isotherms are displaced in the direction of greater relative pressures h of water vapor, and the slope of the central linear part of the isotherm increases. This observation is in qualitative agreement with the results of Dubinin and Zaverina [6], who studied the effect of the adsorption of benzene and dibutyl phthalate on the form of the adsorption isotherm for water vapor on charcoal and observed a displacement toward the right in the isotherms as the amount of adsorbed benzene increased. The adsorption of ethyl chloride depends in a very peculiar way on the value of the relative pressure of water vapor at constant p_2. The curves in Figure 4 show that as h increases the adsorption of C_2H_5Cl at first remains practically constant, or very slowly falls. At h > 0.5, however, there is a sharp fall in the adsorption of ethyl chloride, and for curve 1 the value of a_2 becomes practically zero for h > 0.7, i.e., almost the whole of the ethyl chloride is displaced by water under these conditions. The value of h at which displacement of ethyl chloride from the charcoal is almost complete increases as p_2 rises, as will be seen from Figure 4 on passing from curve 1 to curve 4.

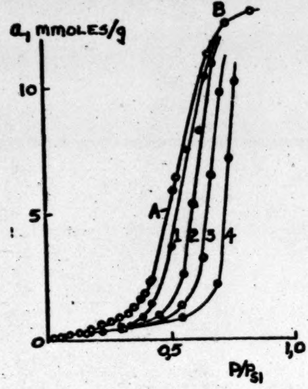

Figure 3. Projection of adsorption isotherm for water on the plane $p_2 = 0$.

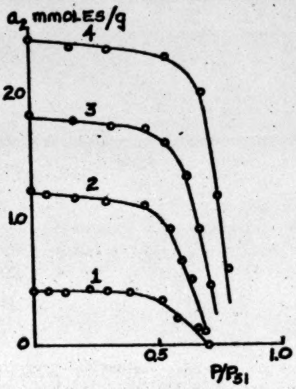

Figure 4. Projection of adsorption isotherm for ethyl chloride on the plane $p_2 = 0$.

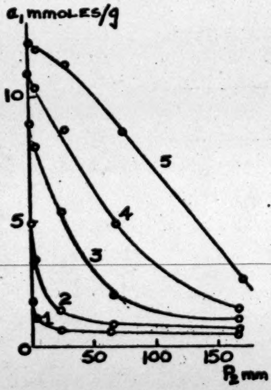

Figure 5. Curves of $a_1 = f_1(p_2)$ for h = const.; 1—h = 0.40; 2—h = 0.50; 3—h = 0.60; 4—h = 0.65; 5—h = 0.70

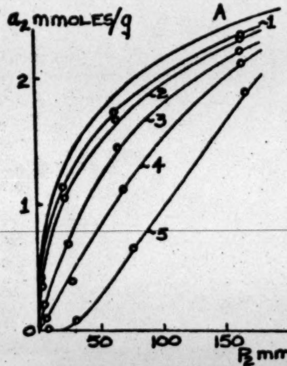

Figure 6. Curves of $a_2 = f_2(p_2)$ for h = const.; A—h = 0; 1—h = 0.40; 2—h = 0.50; 3—h = 0.60; 4—h = 0.65; 5—h = 0.70.

In order to obtain a clearer idea of the forms of the surfaces for the adsorption of the two components (Equations 5), we constructed sections of these surfaces made by the planes $h = p_1/ps_1 = \text{const}$, using the curves in Figures 2, 3, and 4. The families of curves obtained, $a_1 = f_1(C, p_2)$ and $a_2 = f_2(C, p_2)$ (the parameter $p_1 = C$) are given in Figures 5 and 6 respectively.

In Figure 5, when $h = 0.4$ or 0.5 (curves 1 and 2), there is a marked suppression of adsorption of water to be observed already at comparatively low values of p_2, but as further increase in h occurs, the value of p_2 necessary for the displacement of water from the adsorption phase becomes higher and higher. The slope coefficient for curves 1 – 5 at $p_2 = 0$ falls in absolute value in passing from curve 1 to curve 5.

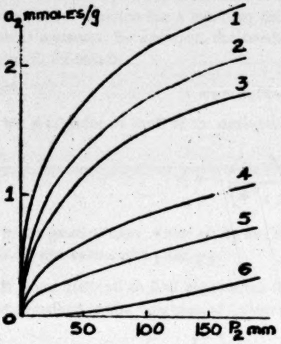

Figure 7. Isotherms $a_2 = f(p_2)$ for $a_1 = \text{const}$; 1 – $a_1 = 0$; 2 – $a_1 = 2.0$; 3 – $a_1 = 5.0$; 4 – $a_1 = 8.0$; 5 – $a_1 = 10.0$; 6 – $a_1 = 12.0$.

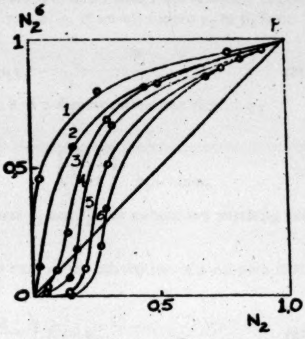

Figure 8. The relation $N_2^\sigma = F(N_2)$ for $P = \text{const}$; 1 – $P = 80$; 2 – $P = 140$; 3 – $P = 180$; 4 – $P = 200$; 5 – $P = 220$; 6 – $P = 240$.

It follows from Figure 6 that for values of h of up to 0.5 the adsorption isotherms for C_2H_5Cl (curves 1 and 2) do not differ greatly in form from the original adsorption isotherm for ethyl chloride in absence of water (curve A). With further rise in h a considerable reduction in the slope of the curve at the origin is to be observed, and at $h = 0.7$ (curve 5) the adsorption isotherm changes the sign of its curvature in its initial section and becomes concave.

In order to obtain an idea of the form of the C_2H_5Cl adsorption isotherms for various constant values of water adsorption, we constructed curves of $a_2 = f(p_2)$ for $a_1 = \text{const}$, on the basis of the curves in Figures 2 – 4. The curves so obtained are shown in Figure 7, and it will be seen that as a_1 increases the adsorbability of ethyl chloride rapidly falls. The change in the form of the adsorption isotherm is, however, slight, and the rapid change in slope at the beginning of the curve is preserved even at $a_1 = 10.0$ mmoles/g. This fact leads us to suppose that even when the adsorption of water is high the charcoal surface remains heterogeneous with respect to ethyl chloride. It will be seen that in the interval $a_1 = 10.0$-12.0 mmoles/g the C_2H_5Cl adsorption isotherm changes its form and becomes concave. It is only at these values of a_1 that ethyl chloride is practically not adsorbed on charcoal at low pressures (p_2) at the temperature of the experiments. It should be noted that the curve corresponding to $a_1 = 12.0$ is less reliable, since it was constructed by the extrapolation of the curves in Figures 3 and 4.

On the basis of these considerations, we may conclude that the system under examination, $H_2O + C_2H_5Cl$, is considerably more complex than the previously studied systems, $CO_2 + C_2H_4$ and $C_2H_4 + C_3H_6$, and in this connection it should be noted that the rule previously found [2, 3] regarding the linearity of the total-adsorption isosteres is not observed in the system $H_2O + C_2H_5Cl$. Similarly, the relation of the molar fraction N_2^σ of ethyl chloride in the adsorption phase to its molar fraction N_2 in the gas phase is considerably more complicated.

Figure 8 shows the relation between N_2^σ and N_2 for various values of constant total pressure P in the gas phase. For $P < 0.5ps_1$ the curves of $N_2^\sigma = F(N_2)$ are very similar to the corresponding curves for the mixtures studied previously, and the selectivity coefficient α_2 for ethyl chloride varies, for example along curve 1, from 30 to 5. With rise in P, however, these curves take up an S-shape with a point of inflexion, and their lower sections are below the diagonal OB, along which $\alpha_2 = 1$. The lower parts of these curves (for example, curve 6) up to the point of intersection with the diagonal correspond to values of $\alpha_2 < 1$ (and therefore to values of the selectivity coefficient for water of $a_1>1$), and the parts of the curves lying above this diagonal correspond to values of $a_2>1$.

We may conclude from an examination of the curves in Figs. 4 and 5 that the adsorption of a mixture of H_2O and C_2H_5Cl is associated with marked competition between the two types of molecules. As p_1 rises (p_2 being maintained constant), displacement of C_2H_5Cl molecules from the charcoal by water occurs (see Fig. 4), and this process may evidently proceed until the whole of the ethyl chloride is displaced. On the other hand, as p_2 rises at constant p_1 (see Fig. 5), displacement of water molecules from the surface phase occurs, but this process, apparently, cannot lead to the complete displacement of water from the charcoal, at least for values of p_2 below 200 mm Hg.

We shall now make a more detailed examination of the stoichiometry of the displacement, i.e., the question of the ratio in which the molecules of one component may replace those of the other in the adsorption phase. This form of the question has a meaning only when definite conditions are laid down with respect to the values of the partial pressures, for example, the condition that p_1 or p_2 = const. Actually, if we eliminate p_1 or p_2 from Equations 5, we obtain

$$a_1 = \varphi_1(a_2, p_2) \quad \text{or} \quad a_2 = \varphi_2(a_1, p_1). \tag{6}$$

We shall refer to each of the derivatives obtained from Equation 6 as a displacement coefficient γ:

$$\gamma_1 = -\left(\frac{\partial a_1}{\partial a_2}\right)_{p_2=\text{const.}} \quad \text{or} \quad \gamma_2 = -\left(\frac{\partial a_2}{\partial a_1}\right)_{p_1=\text{const.}} \tag{7}$$

In the general case, when we do not know the form of the functions $\underline{f_1}$ and $\underline{f_2}$, we cannot say anything beforehand about the values of γ_1 and γ_2.

It is not difficult to find expressions for Equations 6 and 7 for the case of the adsorption of a mixture that may be described in the language of Langmuir's theory:

$$a_1 = -\left(1+\frac{1}{b_2p_2}\right)a_2 + a_m \quad \text{or} \quad a_2 = -\left(1+\frac{1}{b_1p_1}\right)a_1 + a_m \tag{8}$$

and correspondingly

$$\gamma_1 = 1+\frac{1}{b_2p_2} \quad \text{or} \quad \gamma_2 = 1+\frac{1}{b_1p_1}\ . \tag{9}$$

The coefficients γ_1 and γ_2 therefore depend on p_1 or p_2 and on the adsorption coefficients: as $p_2 \to \infty$, $\gamma_1 \to 1$, and as $p_1 \to \infty$, $\gamma_2 \to 1$. Hence, in the case under examination, one molecule of the first component displaces one of the second component, only for $p_2 \to \infty$, i.e., in a saturated monolayer. At lower surface coverage, $\gamma_1>1$ and $\gamma_2>1$. In the coordinates a_2, a_1, the family of curves described by the first of Equations 8 is a ray of straight lines originating in the point (0, a_m). The slope of these lines falls with rise in p_2 and tends to the value -1 as $p_2 \to \infty$. The corresponding ray of lines described by the second of Equations 8 originates in the point (a_m, 0), and the slope coefficient of these lines increases with rise in p_1 and tends to the value -1 as $p_1 \to \infty$.

On constructing the curves $a_1 = \varphi(a_2)$ for the systems studied previously [1-3], we obtained approximately linear curves, and they varied in slope in such a way that the coefficients γ_1 and γ_2 approached the value of unity as p_1 and p_2 increased in value. From the curves in Figs. 5 and 6 we constructed curves showing the dependence of the adsorption of water a_1 on the adsorption of ethyl chloride a_2. The resulting curves for p_1 = const are shown in Fig. 9, and the corresponding curves for p_2 = const are shown in Fig. 10.

As the parameter $h = p_1/p_{s1}$ increases the curve $a_1 = F_1(a_2)$ in Fig. 9 gradually becomes straighter, and its slope increases. The slope of the corresponding curve in Fig. 10 falls with rise in p_2. However, in contrast to the previously examined case of Equations 8 and 9, the limiting value to which the slope coefficient of the linear part of the curve in Fig. 9 tends as p_1 increases is fairly close to -5 (in Figs. 9 and 10 the scale of the abscissa axis is five times as great as that of the ordinate axis). The value to which the slope coefficient of the linear part of the curve in Fig. 10 tends as p_2 increases is also -5 (see the curve corresponding to p_2 = 160). The limiting values of the coefficients γ_1 and γ_2 in the given case are therefore not 1, but 5. In other words, at high pressures five H_2O molecules are needed for the displacement of one C_2H_5Cl molecule.

If we assume that at high pressures p_1 and p_2 corresponding to the limiting value of the γ coefficients we are dealing with spatial displacement from the pores of the charcoal of one liquefied component by another,

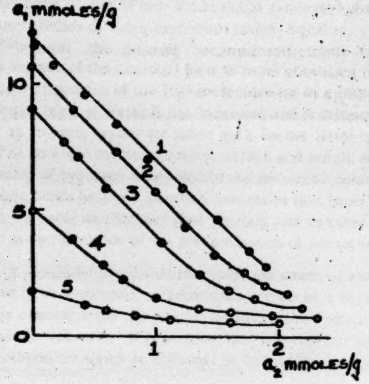

Fig. 9. The relation $a_1 = F_1(a_2)$ ($\underline{h}$ = const); 1) h = 0.70; 2) h = 0.65; 3) h = 0.60; 4) h = 0.50; 5) h = 0.40

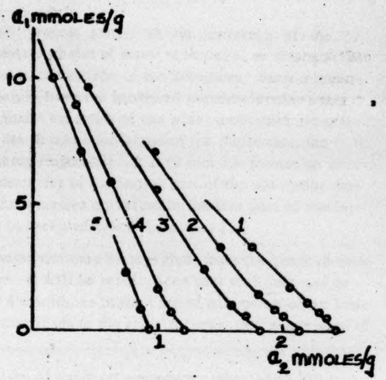

Fig. 10. The relation $a_1 = F_2(a_2)$ (p_2 = const); 1) p_2 = 160; 2) p_2 = 100; 3) p_2 = 60; 4) p_2 = 20; 5) p_2 = 10

also liquefied, component, then the coefficient γ must be equal to the ratio of the molar volumes V_2/V_1 of ethyl chloride and water. Assuming the normal values of the density δ for water and ethyl chloride, we obtain a value of 3.9 for this ratio. It is extremely unlikely that the ratio δ_1/δ_2 in the pores of the charcoal is 1.27 times greater than the corresponding ratio of the normal densities of H_2O and C_2H_5Cl. We therefore consider that the value $\gamma = 5$ contradicts the concept of equivalent-space displacement of one liquid component by another. Moreover, a further argument may be advanced against this concept: the highest relative pressure of ethyl chloride attained in our experiments was 0.033, and at such a low relative pressure, ethyl chloride can definitely not occur in the pores of the charcoal as a liquid phase.

If we assume that water occurs in the adsorption phase as liquid condensed in capillaries, whereas ethyl chloride is adsorbed at the surface of the charcoal, then it is impossible to explain the constancy of γ, since it is obvious that in a system of pores of various dimensions the process of displacement of an adsorbed layer of ethyl chloride by liquid water cannot be characterized by a constant value of γ.

If we regard the sharp rise of the adsorption isotherms for water as the result of capillary condensation, substantial difficulties arise in the explanation of the displacement we have found in curves $\underline{1-4}$ (Fig. 3) in a right-hand direction from the origin, and also of the progressive increase in the steepness of their middle portions. If we apply Thomson's equation to these curves, we shall, of course, obtain a family of various "distribution curves" of pore volume against radius, instead of the single distribution curve that actually characterizes the given porous adsorbent. From the formal point of view, this difficulty can be avoided by ascribing a different value of the contact angle (varying along each curve) to each of the curves in Fig. 3. From our point of view, however, capillary condensation is possible only after the formation of at least a monomolecular adsorbed layer, since the preliminary formation of a meniscus is, of course, bound to occur in this process. If, however, the adsorbent is already covered with a monomolecular layer, it is difficult to imagine that the contact angle can differ from zero.

On account of these considerations, we consider that our results are in conflict with the concept of capillary condensation and that the explanation of the observed phenomena must be based on a different mechanism for the adsorption of water on charcoal, without introduction of the hypothesis of capillary condensation.

It has already been suggested [7] that hydrogen bonds, formed between adsorbed molecules, play an important part in the adsorption of water molecules on the surface of charcoal. It may be supposed that at low surface coverage adsorption is brought about by weak Van der Waals forces between the water molecules and the charcoal surface. As the surface concentration increases, there is an increase in the probability of the formation of complexes consisting of several H_2O molecules united by hydrogen bonds. As is well known, water molecules are not associated in the gas phase, their thermal energy being sufficient to destroy complexes that form. In the surface layer, however, the field of force of the adsorbent stabilizes the complexes formed. As the presence of water vapor increases little islands of two-dimensional condensed phase appear on the charcoal surface: they are formed of fragmentary chains of water molecules linked together by hydrogen bonds.

Whenever the pressure becomes sufficiently high, this process results in the covering of the whole surface of the charcoal by a network consisting of fragmentary chains of water molecules, so arranged that the dipole moments of the H_2O molecules lie in a plane parallel to the surface of the adsorbent. Such a monomolecular layer of water is not localized and is distinct in principle from the localized monomolecular water layer on an ionic crystal (or silica gel); for the latter case the dipole moments of the water molecules are oriented at an angle to the adsorbent surface and repulsive forces are in operation between the molecules, the formation of hydrogen bonds within the monomolecular layer being impossible. It is in fact the formation of hydrogen bonds between adsorbed molecules that leads to the concavity of the initial part of the adsorption isotherm for water on charcoal (and possibly also in other cases), for negative curvature in the first part of the isotherm is an indication of the predominance of attractive forces between adsorbed molecules [5].

It should be noted that the hydrogen atoms of adsorbed molecules may be regarded, from the point of view that we have developed, as adsorption centers of a peculiar type. It will be readily seen that with increase in surface concentration the number of adsorption centers will not diminish, as in the case of adsorption on an ionic crystal, but increase. It is possible that it is this circumstance that leads to the rapid increase in the steepness of the isotherm for water on charcoal in its middle section.

It should be remembered that the isotherm for the adsorption of water on nonporous carbon black [7] is very similar to that for the adsorption of water on charcoal, a fact that indicates an identical mechanism in both cases.

In our opinion, the rapid increase in the adsorption of water on charcoal in the range of $\underline{h} = 0.4\text{-}0.7$ is a change of state in a two-dimensional phase. This two-dimensional condensation process, however, proceeds not at constant pressure p_1, but over a fairly wide range of pressure. The existence of this range may be formally explained by introducing the concept of surface heterogeneity; but there is reason to suppose that the surface of charcoal is very homogeneous with respect to the adsorption of water, since the adsorption potential is determined primarily by the energy of the hydrogen bond, and not by the energy of interaction with the surface. It is possible that even on an ideally homogeneous surface this process of the formation of a condensed two-dimensional phase would take place over a certain range of values of $\underline{h}$.

If we take this mechanism for the adsorption of water on charcoal as a basis, then we must assume that the process leading to the displacement of ethyl chloride by water occurs within a monomolecular layer. It is possible that the equation $\gamma = 5$ is determined by purely energetic considerations. As the heat of adsorption of ethyl chloride on charcoal is about 12 kcal/mole, and the energy of one hydrogen bond in water is about 3.5 kcal/mole, then for $\gamma = 5$ the average number of hydrogen bonds broken per molecule when five H_2O molecules are replaced by one C_2H_5Cl molecule does not exceed $\frac{12}{5 \times 3.5}$, i.e., ≈ 0.75. It may therefore be concluded that the average degree of association of water molecules in the surface layer is greater than two, but probably does not exceed four.

The supposition that the steep rise of the adsorption isotherms for water on charcoal results from a two-dimensional change of state, and not from capillary condensation, permits us to give a qualitative explanation of the displacements in the curves in Fig. 3. It will be evident that the presence of C_2H_5Cl molecules on the surface of the charcoal reduces the probability of the formation of associated complexes $(H_2O)_n$ in the adsorption phase. This results in a displacement of the beginning of the sharp rise in the direction of higher values of $\underline{h}$. Then, as shown above, displacement of C_2H_5Cl molecules occurs, and as a result of this process, the adsorption properties of the surface approximate to those of a surface characterized by isotherm $\underline{A}$ in Fig. 3. From this point of view, the tendency of the curves in Fig. 3 to come closer together as the adsorption of water increases is a natural one.

We will point out also that, if in accord with the concepts just presented, we consider that point $\underline{B}$ on isotherm $\underline{A}$ in Fig. 3 corresponds to a complete monolayer, then, assuming that the area occupied by a water molecule is 10 A^2, we obtain the very reasonable value of $\sim$700 sq.m/g for the specific surface of the charcoal. It should however be emphasized that, although the experimental results for the charcoal studied can be explained without introducing concepts concerning capillary condensation, this does not mean, of course, that the process of two-dimensional change of state of water on charcoal may not be complicated in other cases by simultaneously occuring capillary condensation in accord with the concepts of "forced" capillary condensation developed by Dubinin and Zaverina [8, 9].

The authors have the pleasant duty of expressing their gratitude to M. M. Dubinin and B. V. Ilyin for their constant interest in this work.

SUMMARY

1. A new volumetric-gravimetric method for the measurement of simultaneous adsorption from binary mixtures of gases or vapors on solid adsorbents is described.

2. Measurements have been made of simultaneous adsorption from mixtures of H_2O and C_2H_5Cl on active charcoal at 74° over a range of relative pressure of water vapor of 0-0.85 and over a range of partial pressures p_2 of ethyl chloride of 0-180 mm Hg.

3. The adsorption isotherms for water at constant p_2 are displaced by rise in the value of p_2 to the right from the origin, and the steepness of their linear middle sections increases.

4. Rise in relative pressure h of water vapor to above 0.5 at constant partial pressure of ethyl chloride leads to a sharp fall in the sorption of ethyl chloride. With further rise in h, the ethyl chloride is practically completely displaced from the charcoal by water.

5. An examination has been made of the stoichiometry of adsorptional displacement in the adsorption of binary gas mixtures. It has been shown that on the basis of Langmuir's theory, the displacement coefficient γ should tend to unity as the pressure increases. It has been found that in the adsorption of mixtures of H_2O and C_2H_5Cl on charcoal at high pressures γ approximates to the value 5, so that in adsorptional displacement five H_2O molecules are equivalent to one C_2H_5Cl molecule.

6. The difficulties arising in the interpretation of the results from the point of view of the concept of capillary condensation of water in the given system are pointed out, and one of the other possible mechanisms of adsorption of water on charcoal is examined: it is based on the hypothesis of two-dimensional change of state in the adsorption layer resulting from the formation of hydrogen bonds between adsorbed water molecules.

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ISOMERISM OF THE DIBROMODINITROPLATINATE(II) ION

A. A. Grinberg, A. I. Dobroborskaya, and G. A. Shagisultanova

According to coordination theory, compounds of the type $K_2[PtX_2Y_2]$, in which X and Y are acid residues, should exist in two geometrically isomeric forms of cis and trans structure:

$$\begin{bmatrix} X & & Y \\ & Pt & \\ X & & Y \end{bmatrix} K_2\,\text{(cis)} \quad \text{and} \quad \begin{bmatrix} X & & Y \\ & Pt & \\ Y & & X \end{bmatrix} K_2\,\text{(trans)}$$

Many examples are known of similar isomerism in compounds of the type $[Pta_2X_2]$, in which a is an amine and X an acid residue, and also in compounds of the type $[Pta_2a'_2]X_2$, in which a and a' are different amine molecules [1]. However, for compounds in which only the usual acid residues are attached to platinum, such isomerism has not yet been observed. This fact was at one time regarded as an argument in favor of the tetrahedral, rather than the planar, structure for compounds of this type, and it later came to be regarded as a result of the high mobility of coordinated acid residues and the associated tendency to undergo rearrangements.

In 1951 analogous isomerism among quadrivalent platinum compounds was described by Babaeva, who investigated compounds of composition $K_2[Pt(NO_2)_3Cl_3]$ [2].

In the present investigation it has been shown that the compound of composition $K_2[Pt(NO_2)_2Br_2]$ can be obtained in two isomeric forms. It is true that we have not yet succeeded in effecting the complete separation of the isomers and their preparation in the pure state, but the reactions of the salt $K_2[Pt(NO_2)_2Br_2]$ indicate that it is a mixture of two isomers standing in cis-trans relationship to one another.

EXPERIMENTAL

Isomeric forms of the compound $K_2[Pt(NO_2)_2Br_2]$ were obtained by the reaction:

$$K_2[Pt(NO_2)_4] + K_2[PtBr_4] \rightarrow 2K_2[Pt(NO_2)_2Br_2].$$

When equimolecular proportions of $K_2[Pt(NO_2)_4]$ and $K_2[PtBr_4]$ were mixed and heated in a water bath for about thirty minutes, the characteristic color of bromoplatinate(II) slowly disappeared and a golden-yellow solution was obtained, from which, on evaporation, a salt of composition $K_2[Pt(NO_2)_2Br_2]$ separated. When the solution of $K_2[Pt(NO_2)_2Br_2]$, obtained by reaction of $K_2[Pt(NO_2)_4]$ and $K_2[PtBr_4]$ was treated with ammonia, fairly rapid precipitation of a colorless crystalline substance occurred. If this was rapidly filtered off under suction, a second crop of crystals of somewhat different form began to separate after a certain time.

Analysis indicated that both fractions of the salt obtained in this way had a composition corresponding to the formula $[Pt(NH_3)_2(NO_2)_2]$.

Analysis of Fraction I

Found %: Pt 60.64; 60.34

$[Pt(NH_3)_2(NO_2)_2]$. Calculated %: Pt 60.78

Analysis of Fraction II

Found %: Pt 60.71; 60.52; 59.65

$[Pt(NH_3)_2(NO_2)_2]$. Calculated %: Pt 60.78

It is clear from this that reaction with NH_3 proceeds mainly as follows:

$$K_2[Pt(NO_2)_2Br_2] + 2NH_3 \rightarrow [Pt(NH_3)_2(NO_2)_2] + 2KBr^*$$

The configurations of the salts present in the two fractions were determined by Kurnakov's thiourea reaction. It was found that Fraction I consisted of trans-dinitrodiammineplatinum, and Fraction II of a mixture of cis- and trans-dinitrodiammineplatinums.

In addition, a new reaction was applied for the chacterization of the configurations: it consisted in treatment of the preparation of dinitrodiammineplatinum under test with a few drops of phenolphthalein and a considerable excess (10 moles per mole of salt) of potassium iodide. Trans-dinitrodiammineplatinum gave a yellow precipitate of trans-$[Pt(NH_3)_2I_2)]$ (first of all the colorless solution turned yellow).

Analysis of the yellow salt

Found %: Pt 40.50; 40.54

$[Pt(NH_3)_2I_2]$. Calculated %: Pt 40.41

Under the same conditions the cis isomer gave a bright-red solution; evidently, ammonia, labilized by the nitro group situated at the opposite side, was eliminated from the inner sphere.

The fact that the action of ammonia on a solution $K_2[Pt(NO_2)_2Br_2]$ yields not the cis isomer, as would be expected on the basis of Peyrone's rule, but a mixture of both isomers in which the trans form actually predominates, is extremely interesting.

There may be two explanations of this position: 1) it may be supposed that the two isomers are formed by the action of ammonia on one single salt present in the solution, and 2) it may be supposed that two isomers of the salt $K_2[Pt(NO_2)_2Br_2]$, are present in the solution, and these react in different ways with ammonia. The second supposition implies that the salt of composition $K_2[Pt(NO_2)_2Br_2]$ is actually able to exist in cis and trans forms.

In order to decide which supposition is correct, we attempted to effect some separation, if only partial, of the supposed isomers of composition $K_2[Pt(NO_2)_2Br_2]$ by means of fractional crystallization. This operation was carried out as follows: A solution of the salt $K_2[Pt(NO_2)_2Br_2]$, prepared as already described, was evaporated down on a water bath until crystals began to separate, and was then cooled strongly by immersion in ice. The fraction of crystals that separated was filtered off under suction. A further batch of crystals was obtained from the mother liquor by a similar method. The filtered fractions were washed with alcohol and dried at 90-95°.

Fraction I, obtained in this way, was a light-yellow crystalline substance, and Fraction II was somewhat darker in color (with an orange tinge) and turned appreciably darker in the drying process. The two fractions of crystals showed practically no difference in analysis.

Analysis of Fraction I

Found %: $(Pt + K_2SO_4)$ 70.65; 70.79; 70.66; 70.68; Pt 37.43; Br 30.28
Calculated %: $(Pt + K_2SO_4)$ 70.34; Pt 37.18; Br 30.42

Analysis of Fraction II

Found %: $(Pt + K_2SO_4)$ 70.65; 70.60; 70.83; 70.89; Pt 36.87; Br 29.98
Calculated %: $(Pt + K_2SO_4)$ 70.34; Pt 37.18; Br 30.42

The analyses show that both fractions are of composition $K_2[Pt(NO_2)_2Br_2]$. We then proceeded as follows: we took equal amounts (0.25 g) of the two fractions and dissolved them in equal amounts of water (2.5 ml). The solutions obtained were somewhat different in color, the solution of Fraction II having an orange tinge.

Ammonia was added to the solutions in the amounts calculated for diammine formation (about 0.1 ml of 18% ammonia solution), and decolorization and precipitation of dinitrodiammineplatinums occurred. Decolorization was considerably slower in the solution of Fraction II.

In both cases two separate fractions of dinitrodiammineplatinum were separated (four batches of salt altogether). Samples from all the batches were analyzed for platinum content, and the results corresponded to the composition $[Pt(NH_3)_2(NO_2)_2]$.

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* At the same time a very small amount of $[Pt(NH_3)_2NO_2Br]$ is formed.

Analysis of Fractions I and II of the ammine from the first fraction of $K_2[Pt(NO_2)_2Br_2]$

Found %: Pt 60.84; 60.19

$[Pt(NH_3)_2(NO_2)_2]$. Calculated %: Pt 60.78

Analysis of Fractions I and II of the ammine from the second fraction of $K_2[Pt(NO_2)_2Br_2]$.

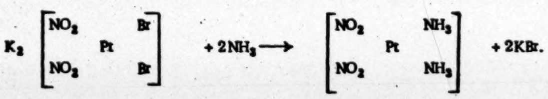
Found %: Pt 60.44; 60.42

$[Pt(NH_3)_2(NO_2)_2]$. Calculated %: Pt 60.78

Tests on all batches were made with the aid of the above-described KI/phenolphthalein reaction, and it was found that the first fractions of $[Pt(NH_3)_2(NO_2)_2]$ obtained from the two fractions of $K_2[Pt(NO_2)_2Br_2]$ gave only a weak pink coloration. The behavior of these fractions in this reaction was not very characteristic. A very distinct difference in behavior in this reaction was shown by the second fractions of the ammines, and the results of these tests were very reproducible. The second fraction obtained from the more difficultly soluble crystals of $K_2[Pt(NO_2)_2Br_2]$ gave a feeble "cis reaction", whereas the corresponding fraction from the readily soluble crystals of $K_2[Pt(NO_2)_2Br_2]$ gave a very intense reaction under the same conditions.

These results show that the salt $K_2[Pt(NO_2)_2Br_2]$ does undergo partial separation into two modifications in the process of fractional crystallization, the more soluble product being enriched in cis isomer. It is evident that both theoretically possible forms are produced in the reaction $K_2[Pt(NO_2)_4]$ with $K_2[PtBr_4]$. This follows directly from Chernyaev's trans-effect principle and the relative closeness of the values of the trans effects of the two acid residues. These forms are bound to differ in their general physical properties and, in particular, their solubilities. Their separation may be complicated by their interconversion, which is possible in principle. Thus, it might be expected that in the process of fractional crystallization the more readily soluble isomer might be transformed into the less soluble form. If the rate of such conversion is sufficiently great, then the more soluble isomer may be largely removed from the solution. Our results show that under our conditions of fractional crystallization a sufficient amount of cis isomer nevertheless remained for it to be detected by the method described.

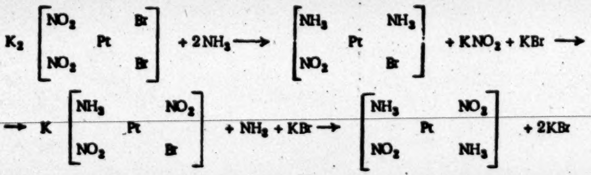
The action of ammonia on a solution of potassium dibromodinitroplatinate(II) containing both isomeric forms may proceed as follows: cis-Dinitrodiammineplatinum may be formed in the normal way from cis-$K_2[Pt(NO_2)_2Br_2]$ according to the equation:



$$K_2\left[\begin{matrix} NO_2 & & Br \\ & Pt & \\ NO_2 & & Br \end{matrix}\right] + 2NH_3 \longrightarrow \left[\begin{matrix} NO_2 & & NH_3 \\ & Pt & \\ NO_2 & & NH_3 \end{matrix}\right] + 2KBr.$$

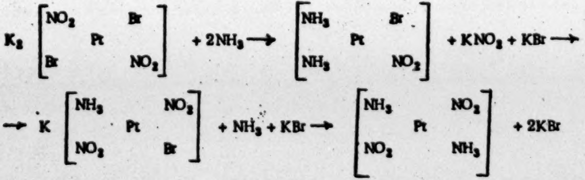
The trans-dinitrodiammineplatinum may, however be formed in several ways. It may, for example, arise from cis-$K_2[Pt(NO_2)_2Br_2]$ via intermediately formed cis-bromonitrodiammineplatinum, which is converted via potassium trans-bromodinitroammineplatinate(II) into the trans-dinitrodiammine isomer.

trans-Dinitrodiammineplatinum may be formed also via the same intermediate products from potassium trans-dibromodinitroplatinate(II). Equations representing these respective changes are:



$$K_2\left[\begin{matrix} NO_2 & & Br \\ & Pt & \\ NO_2 & & Br \end{matrix}\right] + 2NH_3 \longrightarrow \left[\begin{matrix} NH_3 & & NH_3 \\ & Pt & \\ NO_2 & & Br \end{matrix}\right] + KNO_2 + KBr \longrightarrow$$

$$\longrightarrow K\left[\begin{matrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & Br \end{matrix}\right] + NH_3 + KBr \longrightarrow \left[\begin{matrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & NH_3 \end{matrix}\right] + 2KBr \quad (1)$$



$$K_2\left[\begin{matrix} NO_2 & & Br \\ & Pt & \\ Br & & NO_2 \end{matrix}\right] + 2NH_3 \longrightarrow \left[\begin{matrix} NH_3 & & Br \\ & Pt & \\ NH_3 & & NO_2 \end{matrix}\right] + KNO_2 + KBr \longrightarrow$$

$$\longrightarrow K\left[\begin{matrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & Br \end{matrix}\right] + NH_3 + KBr \longrightarrow \left[\begin{matrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & NH_3 \end{matrix}\right] + 2KBr \quad (2)$$

SUMMARY

1. It has been shown that, when equimolecular amounts of $K_2[PtBr_4]$ and $K_2[Pt(NO_2)_4]$ react, the product has the composition $K_2[Pt(NO_2)_2Br_2]$, and behaves like a mixture of geometric isomerides.

2. Treatment of a solution of the salt $K_2[Pt(NO_2)_2Br_2]$, obtained as indicated above, with ammonia yields trans-dinitrodiammineplatinum containing cis-dinitrodiammineplatinum impurity.

3. A new reaction has been applied for the distinguishing of the two isomers of dinitrodiammineplatinum.

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ELECTRONIC PROCESSES IN CHEMISORPTION

COMMUNICATION 2*

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In the preceding paper [1] we postulated that the adsorbent surface is an ideal plane. Also, we considered that a one-electron bond between an adsorbed atom and the surface is so weak (in comparison with a two-electron bond), that its effect can in general be neglected.

In this paper we shall examine the mechanism of chemisorption without making these two assumptions. The paper, like the preceding one [1], is a condensed (qualitative) exposition of the main results of a series of theoretical investigations carried out by the author.

"Thermal Disorder" on the Surface of a Crystal, and its Role in Adsorption

Let us examine a real surface, which is distinguished from an ideal surface by the presence of defects of various kinds which disturb the strictly periodic structure of the surface. We must here distinguish between macro- and micro defects.

A macro defect is a disturbance over a region having dimensions considerably greater than those of the unit cell of the crystal; for example, fissures in the crystal surface and macroscopic occlusions. We shall not examine such defects here.

A micro defect is a disturbance having dimensions of the same order as those of the unit crystal cell. When there is a micro defect, the periodic structure of the surface is practically re-established at a distance equal to several times the lattice constant. We shall confine ourselves here to a consideration of defects of this sort. In other words, we shall be dealing not with a model of an ideal surface, as in the previous paper [1], but with a somewhat idealized model of a real surface [2, 3].

As examples of micro defects present on all real surfaces we may note the following: a) a vacant lattice point formed by the removal of an ion from the surface layer of the lattice (Fig. 1, a); b) an ion or atom normally found in the lattice, but lying on the surface (rejected from a lattice point, or introduced from outside) (Fig. 1, b); c) a foreign atom or ion lying on the surface (Fig. 1, d); or situated at a lattice point, i.e., replacing an ion proper to the lattice (Fig. 1, c).

The presence of defects is a characteristic of what may be termed "disorder" at the surface of the crystal. In disorder as a whole, two components must be distinguished: "biographic" and "thermal" components. "Biographic disorder" is that part of disorder that is preserved at the absolute zero of temperature; it is the irreversible part. The degree of "biographic disorder" is determined by the technology of the sample — the whole of its previous history; it is the disorder acquired by the lattice "from birth", as it were. On this component of disorder there is superposed the reversible "thermal disorder", which increases as the temperature rises. In fact, as the temperature rises, there is an increase in the dissociation of the ions from the lattice points into the intermediate space, and also in their ejection onto the surface of the crystal. On the other hand, as the temperature falls the degree of order in the lattice increases: ions return to their lattice points and the degree of disorder diminishes. The lattice itself can thus both produce and efface defects: this is a fundamental point.

In the electron economy of the lattice defects play a dual part: some of them are electron acceptors, i.e., traps for conductivity electrons; others are electron donors, i.e., the reservoir from which the conductivity zone obtains free electrons. Defects, therefore, play the part of localization centers for free electrons or for free holes.

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*Paper read at a conference on heterogeneous catalysis in Moscow on January 28, 1953.

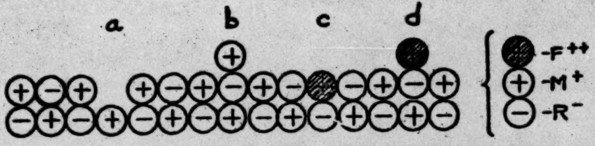

Fig. 1.

In chemical language: they are localization centers for free valencies, which wander over the crystal surface. In other words, such wandering valencies become attached at places where the periodic structure of the lattice is disturbed, and are localized at these places.

Surface defects may therefore be regarded as adsorption centers. Such a concept is in accord with Taylor's views and may be regarded to some extent as an interpretation of them: according to Taylor adsorption centers are formed by geometric heterogeneities on the surface, and on our idealized surface such heterogeneities are represented by micro defects.

Under normal conditions, the concentration of free electrons is negligibly low compared with that of localized electrons, i.e., the electrons held at defects. In other words, the number of freely wandering (nonlocalized) valencies is low compared with the number of valencies localized at defects. Under these conditions adsorption on free electrons may be neglected in comparison with adsorption on defects. Adsorption on defects (one- and two-electron bond) has been examined by Bonch-Bruevich [4].

It must be noted that the presence of defects on the surface does not imply energetic heterogeneity of the surface, which is associated with the presence of adsorption centers of various kinds. If, in fact, the adsorption centers are defects of only one particular kind, all characterized by the same heat of adsorption q, then our surface is energetically homogeneous from the adsorption point of view.

The adsorption properties of such a surface have been investigated in detail. Adsorption isotherms for such a surface have been found to have a Freundlich form (the index having the value of 1/2). The differential heat of adsorption is a function of the surface coverage, and the adsorption kinetics are also typically non-Langmuir. In other words, such a surface, which is homogeneous in the usual sense of the word (adsorption centers of only one kind!), behaves as a heterogeneous surface.

The cause of this behavior is that the number of adsorption centers on our surface does not remain constant, but changes with temperature. In other words, the specific non-Langmuir properties of the surface are determined by the thermal component of the disorder. If thermal disorder is neglected, only biographic disorder being retained, then all formulas are automatically transformed into the usual formulas of Langmuir theory. Actually, adsorption centers, treated as micro defects of the surface or, more exactly, as electrons (or free valencies) localized at these defects, participate not only in adsorption and desorption reactions, but also, of course, in the reactions of production and effacement of centers by the lattice itself. These reactions proceed on the surface along with the adsorption and desorption reactions.

Consideration of these reactions implies consideration of thermal disorder, and ignoring them implies a return into the framework of Langmuir theory, which relates to a constant number (independent of temperature) of adsorption centers, i.e., ignores thermal disorder in comparison with disorder of biographic origin.

"Weak" and "Strong" Bonds in Chemisorption

We shall now return to the picture of the ideal surface. As we have seen [1], two types of bond are possible between a univalent electropositive atom A and the adsorbent surface.

1. There is the one-electron (comparatively weak) bond produced by the drawing of a valency electron of atom A out of the atom on to the lattice. With respect to a free electron of the lattice, which travels in the surface conductivity zone, the atom A adsorbed in this way constitutes a "trap", i.e., acts as a foreign acceptor, and may be represented in the energetic spectrum of the crystal as a local acceptor level (Fig. 2, a).

2. If the adsorbed atom A, bound to the surface by this one-electron bond, captures a free electron of the lattice, the one-electron bond passes, as has been shown, into a stronger, two-electron bond.

The "strengthening" of the bond may be regarded as the saturation of the valency of atom A resulting from the acquiring of the free electron from the lattice. This "strengthening" of the bond is represented on Fig. 2, a by the appearance of an electron in the local level of A. Electronic processes at the surface of the crystal may thus be described in the language of the energy scheme for the foreign semiconductor, which is represented in Fig. 2, a.

In the preceding paper we neglected the "weak" (one-electron) bond in comparison with the "strong" (two-electron) bond. We shall now examine the more general case. We shall consider that the chemically adsorbed atom may have a "weak" or a "strong" bond with the surface [5].

Transitions are possible between these states. These transitions are regulated by the "electron-hole" gas on the crystal surface. Let us turn to Fig. 2, b. The curves represent diagrammatically the energy W of the system as a function of the distance r of the atom A from the surface. The different curves correspond to different electronic states of the system. Curve aa is the adsorption curve on the unactivated crystal, i.e., on a crystal that contains no free electrons and holes. Curve bb is curve aa displaced upward and parallel to itself. It corresponds to adsorption on an activated crystal containing a free electron (in the surface conductivity zone) and a corresponding free hole (in the normal surface zone).

Curves aa and bb correspond to "weak" (one-electron) adsorption. Curve cc corresponds to adsorption by a "strong", two-electron bond. The transition from curve bb or aa to curve cc is associated with the "strengthening" of the bond between the atom A and the surface. These transitions are shown respectively by the arrows 1 and 2 on Figures 2, a and b The reverse transitions (1' and 2') represent "weakening" of the bond.

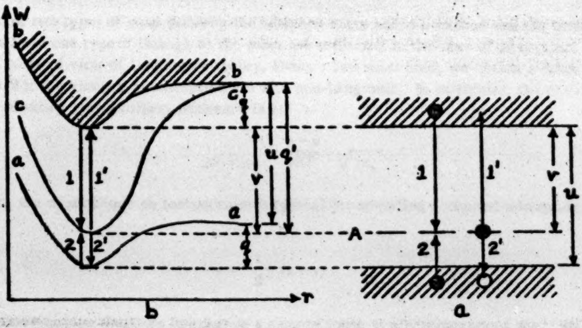

Fig. 2.

The "strengthening" of a bond is therefore accompanied by the disappearance of a free electron from the conductivity zone (transition 1) or the formation of a free hole in the normal zone (transition 2). "Weakening" of a bond, on the contrary, is characterized by the appearance of an electron in the conductivity zone (transition 1') or the filling of a hole in the normal zone (transition 2'). Bond "strengthening" and "weakening" result from electron exchange with the surface.

At equilibrium, a definite fraction of the adsorbed atoms are in the state of "strong" adsorption, and the remainder are in the state of "weak" combination with the surface. Let N be the total number of adsorbed atoms, and N' the number of atoms in the state of "strong" adsorption. We shall refer to the quantity

$$\eta = \frac{N'}{N} \qquad (1)$$

as "degree of combination"; it represents the fraction of the total number of adsorbed atoms that are "strongly" adsorbed, or, in other words, the probability that a given adsorbed atom will have a "strong" linkage with the surface. At the same time η characterizes the relative mean life of the atom in the "strongly" adsorbed state.

The value of η is determined by the concentration of electron gas at the surface of the crystal; we shall denote this concentration by n, and v will be the "affinity energy" of the adsorbed atom A for a free electron of the lattice (Fig. 2, a). The relation between η and n is given by the formula:

$$\eta = \frac{1}{1 + \frac{c}{n} e^{-\frac{v}{kT}}}. \tag{2}$$

The greater, therefore, the concentration of electron gas (at the given temperature), the greater the fraction of adsorbed atoms that is to be found in the "strongly" adsorbed state (we are at present considering electropositive univalent A atoms).

On the other hand, the concentration of electron gas, other things being equal, depends on the coverage of the surface with adsorbed atoms, and η is therefore a function of the coverage. For not too small coverages we have:

$$\eta = \sqrt{\frac{c'}{N} e^{-\frac{u-v}{kT}}} \tag{3}$$

We see that the "degree of combination" of a given atom becomes less as new atoms take their places on the surface. Every adsorbed atom "feels", as it were, the presence on the surface of all the remaining atoms, even though there is no direct interaction between the adsorbed atoms (we ignore it in the calculation). We are dealing here with a special type of interaction resulting from electron exchange with the surface, an interaction that is transmitted by the electron gas.

The presence of two types of bond between the adsorbed atom and the surface and the possibility for an adsorbed atom to pass from one type of linkage to the other are reflected in the laws of adsorption. At low coverage, at which, from the point of view of Langmuir's theory, Henry's law must hold, we obtain a Freundlich isotherm (with an index of 1/2); the kinetics of adsorption are also non-Langmuir. In particular, the coverage of the surface by "strongly" adsorbed atoms follows Benham's law:

$$N' = Ae^{-\frac{u-v}{2kT}} \sqrt{pt}, \tag{4}$$

and, as will be seen, the dependence on temperature is typical for so-called activated adsorption, the activation energy being

$$\epsilon = \frac{1}{2}(u-v)$$

Our homogeneous surface therefore behaves in a certain sense as a heterogeneous one. We are concerned here with heterogeneity of a special type. Our surface actually contains adsorption centers of only one particular type (M^+ ions of the surface layer serve as centers of this sort). Each adsorption center may, however, be bound to any given adsorbed atom by one of two different types of bonds, and in the course of the life of the atom in the adsorbed state the character of its linkage with the given adsorption center may vary.

The departures from the Langmuir laws may be treated as a manifestation of this peculiar type of heterogeneity. On the other hand, these departures may be treated as the result of the special type of interaction between the adsorbed atoms which we have already discussed, namely, interaction effected by means of the electron gas at the surface of the crystal. The concepts of "interaction" and "heterogeneous surface", therefore, in a certain sense merge together. In other words, when electron exchange reactions are taken into account, the distinction between these concepts becomes blurred: this peculiar kind of heterogeneity and this peculiar kind of interaction present themselves as two aspects of one and the same thing—electron exchange processes.

If we ignore these processes, i.e., put $\bar{\eta} = 0$, our formulas are automatically converted into the corresponding Langmuir formulas. The surface becomes a purely Langmuir surface. These processes, however, cannot be ignored, for electron exchange reactions have heats of reaction of the same order of magnitude as those for adsorption (the energies u, v, and q in Fig. 2 have values of the order of tenths of an electron-volt).

Reactivity of Chemically Adsorbed Atoms

The presence of bonds of two types between adsorbed atoms and the surface is of great importance in catalysis. A given atom differs in reactivity according to the state, "strong" or "weak", of its linkage with the surface. In the first case its valency is saturated, and in the second case its valency remains unsaturated. We shall suppose (this is the simplest supposition) that an atom is reactive only while its valency is unsaturated. Atoms, therefore, that are "strongly" bound to the surface do not participate in reaction.

The reactivity of an adsorbed atom may be characterized by the quantity

$$1-\eta = \frac{N-N^{-}}{N} \qquad (5)$$

This quantity is the probability that an adsorbed atom will be found in the reactive condition, and at the same time it indicates the fraction of the total number of adsorbed atoms that may participate in reaction, i.e., may be found in a "weak" state of linkage to the surface. It will be seen (from Equation 2) that the reactivity is the lower, the higher the concentration of the electron gas on the crystal surface (other conditions being equal).

Up to now we have considered a univalent electropositive atom, but these considerations can be applied also to any radical having one positive valency. They may be applied also the case of a univalent electronegative atom, or a radical having one negative valency; in this case, however, the word "electron" must be replaced everwhere by the word "hole". Hence, the reactivity of an adsorbed electronegative atom is the lower, the higher the concentration not of the electron gas, but of the "hole" gas on the crystal surface (other conditions being equal).

It should be noted that in the case of thermal equilibrium the product of the concentrations of the electron gas and of the "hole" gas is always a constant for a given crystal at a given temperature. Hence, the factors leading to the enrichment of the electron gas lead to impoverishment of the "hole" gas, and conversely. The introduction of foreign matter (acceptor or donor) into the crystal constitutes such a factor.

Factors that intensify the reactivity of electropositive atoms (radicals) suppress the reactivity of electronegative atoms (radicals).

As we have already noted, a free electron on the surface of the crystal may be treated as an unsaturated positive valency. Analogously, a free hole may be treated as a negative valency. Under normal conditions, hence, there are a certain number of free positive and negative valencies on the crystal surface. The concentrations of these valencies are respectively equal to those of the electron and hole gases.

The number of such valencies changes with changing conditions (for example, increases with rise of temperature) and may be artificially increased or reduced as the result of external action on the crystal. This behavior is characteristic for the surface of an ionic crystal. Another characteristic feature is that not every free valency is localized: it may wander freely on the surface.

If there are defects on the surface (of "thermal" or "biographic" disorder), then, as we have seen, wandering valencies may be trapped (localized) at these defects, and, on the other hand, valencies localized at defects may escape, i.e., become delocalized. When a wandering free valency meets the unsaturated valency of an adsorbed atom (or radical), mutual valency saturation occurs, this being accompanied by localization of the wandering valency and the transition of the adsorbed atom (radical) into a state of "strong" linkage with the surface (i.e., to the loss of its reactivity).

Up to now we have considered atoms or radicals that have unsaturated valencies in the free state. Such atoms or radicals may appear on the surface in the course of the adsorption of a saturated molecule, i.e., a molecule having no free valencies, when the adsorption of such a molecule is accompanied by its dissociation, as often occurs.

Let us examine a molecule AB formed form two atoms, or groups of atoms, A and B linked together by a single bond (Fig. 3, a). When such a molecule is adsorbed, the bond linking these two groups of atoms in the molecule may be disrupted by a free electron (or, in other cases, by a free hole) of the crystal lattice. In other words, an encounter with a free electron (or with a free hole) may lead to the dissociation of the molecule. One

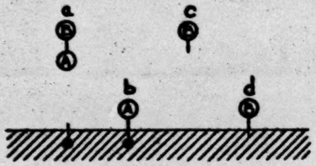

Fig. 3.

of the dissociation products, the radical A for example, is then found to be adsorbed and attached to the surface by a "strong" bond formed with the participation of the free electron or hole that caused the dissociation and captured the radical A (Fig. 3, b). The other dissociation product, the radical B for example, preserves its unsaturated valency and passes into the gas phase (Fig. 3, c), or is adsorbed on the surface, attaching itself by a "weak" bond (Fig. 3, d). The net result is that there appear on the surface the adsorbed radicals A and B in the state of "strong" and "weak" linkage and capable of transition from one state to the other, a state that may be described as the localization and delocalization of an electron or hole, i.e., of a positive or negative valency belonging to the crystal surface.

Reactions occurring on the crystal surface may therefore be regulated by an electron or hole gas. Some stages of reaction may be speeded up and others may be slowed down, depending on the rise in the concentration of the electron gas or the diminution in that of the hole gas. From this there arises a possible mechanism for the action of foreign matter on the activity of a catalyst [6, 7, 8]. The introduction of foreign matter, in fact, changes the concentrations of the electron and hole gases, and as a result the contamination must affect the reactivity of adsorbed atoms (radicals). It should be noted that adsorbed atoms themselves, and molecules participating in reaction or appearing as products of reaction, act as foreign substances on the crystal surface (i.e., affect, as we have seen, the concentration of the electron and hole gases). Reactions occurring on the surface, therefore, may retard themselves (autopoisoning) or accelerate themselves (autopromotion). It should be noted also that this electronic mechanism for the action of foreign material does not require that direct contact should occur between reacting atoms on the one hand, and foreign atoms on the other. The effect of foreign matter is transmitted over a distance. Here we again meet a peculiar type of interaction effected by means of an electron or hole gas.

SUMMARY

1. Theoretical calculations, the results of which have been given here briefly in qualitative fashion, have been made with the object of discovering the elementary (micro-scale) mechanism of a phenomenon. Being concerned with a micro mechanism, these calculations are in their essence quantum-mechanical calculations, and it is this circumstance that determines the most characteristic features of the theory developed. One such characteristic feature is that the theory must operate with simplified and schematized models: with models that lend themselves to quantum-mechanical calculation. The fundamental features of the mechanism then become manifest in their clearest and least obscured form.

2. Another characteristic feature is that, while attempting to explain experimentally observed regularities and to discover the possible source of these regularities, the theory leads us to completely new ideas and concepts which did not figure previously in theories of adsorption. This is again the result of the quantum-mechanical approach to the problem.

3. Finally, for the theory of chemisorption, developed from this aspect, as has been done here, it is characteristic that its basis is the modern theory of solids and that it utilizes the concepts and apparatus of the modern theory of solids. The entry of the theory of solids into the adsorption and catalysis field, i.e., into the territory of physical chemistry, is necessary and inevitable for the creation of a micro-scale theory of chemisorption. The theory of chemisorption, of course, is still not a theory of catalysis, but it forms the first step in the direction of the creation of a theory of catalysis: its ideas and concepts form the foundation on which a theory of catalysis may be built.

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SOLUBILITY OF THE ELEMENTS IN CHROMIUM

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The metal chromium is an element of Group VI of Mendeleev's periodic system of elements, its closest analogs being molybdenum and tungsten. Owing to their high melting points, great strength, and good chemical stability, chromium and its analogs are of considerable interest for the preparation of alloys of practical importance. Chromium, molybdenum, and tungsten alloys, as also the now widely used alloys having an iron, nickel, or other base, are capable of wide application in a number of branches of our technology.

Chromium, like many other metals, by interaction with other metals, or in some cases metalloids, is able to form solid solutions and metallic compounds. The character of the chemical interaction between different metals is determined experimentally by the construction and study of the phase diagrams of the metal systems. We have already published a review of investigations (up to 1953) on the phase diagrams of chromium systems [1].

The crystallographic regularities that are observed now permit us to examine questions relating to the solubility of elements in metals from a general point of view. The circumstances determining the ability of metals to form solid solutions are as follows [2]: 1) closeness in the chemical properties of the elements, which is to be related to their positions in the periodic system; 2) small differences in interatomic distances, i.e., 8-10% for unlimited solid solutions (i.e., formed in all proportions) and 14-16% for limited solid solutions; 3) isomorphism of the crystal lattices of the metals (for formation of unlimited solid solutions).

By applying these conditions we may predict the possibility of the formation of solid solutions between the metals, including chromium. On the basis of the examples afforded by our study of the solubility of the elements in iron [3] and nickel [4, 5], we have demonstrated the existence of the appropriate functional relationship to the factors cited above in the case of the formation of iron and nickel solid solutions. A similar type of relationship in the formation of solid solutions has been observed previously for aluminum [6], copper [7], magnesium [8], and other metals.

Let us examine the solubility of the elements in chromium, following the periods and groups of Mendeleev's periodic system. Table 1 contains information on the differences in atomic diameter between these elements and chromium, and, in the cases where experimental data are available, the solubilities of the elements in chromium are given (at the final temperature of the crystallization).

Data relating to the distribution of elements in the periodic system — which determine the differences and similarities in the chemical properties of the atoms and in their crystal structure — permit us to reach definite conclusions concerning the solubility of the elements in chromium. The elements of Periods I and II — H, Li, Be, B, C, N, and O — are, with the exception of beryllium, characterized by relatively great differences in atomic diameter (from that of chromium) (Table 1). Accordingly, even if hydrogen, with its small atomic diameter, should be found to give solid solutions of insignificant concentration with chromium, then they will only be of an intrusion type. Hydrogen absorbed under the conditions of the electrolytic method for preparing chromium is almost completely removed in a subsequent high-temperature treatment in high vacuum. One of the methods of refining electrolytic chromium is based on this circumstance [10].

This indicates the weakness of the bond between hydrogen atoms and chromium in the solid state and the absence of stable solid solutions of hydrogen in chromium. Lithium, which has a high atomic diameter, greatly different (21.8%) from that of chromium, and which occupies a place far removed from that of chromium in the periodic system, not only does not form solid solutions with chromium, but, in general, does not react with it either in the liquid (molten), or in the solid state. Lithium forms neither solid solutions nor compounds with chromium. The absence of chemical reaction with chromium is characteristic for all the analogs of the lithium, the alkali metals of Group I (Na, K, Rb, and Cs). They, like lithium, neither mix with chromium in the liquid state not give solid solutions with it.

TABLE 1

Solubility of the Elements of the Periodic System in Chromium

Period	Element	Atomic diameter (A)	Atomic diameter difference from that of Cr (%)	Solubility at final temperature of crystallization wt-%	Solubility at final temperature of crystallization atom-%	Supposed solubility
1	2	3	4	5	6	7
I	H	1.2	53.2	Unknown		Insoluble
II	Li	3.13	21.8	Unknown		Insoluble
	Be	2.25	12.4	–	9.3	–
	B	1.94	24.5	Unknown		Very limited solubility
	C	1.54	40.0	Unknown		B >C
	N	1.42	44.7	Unknown		C > N
	O	1.32	48.6	Unknown		N >O
III	Na	3.83	49.0	Unknown		Insoluble
	Mg	3.20	24.5	Unknown		Insoluble
	Al	2.80	8.9	29.0	44.11	–
	Si	2.34	8.9	10.0	17.07	–
	P	2.20	14.4	Unknown		Limited solubility
	S'	2.0	22.2	Unknown		Very limited solubility
IV	K	4.76	85.2	Unknown		Insoluble
	Ca	3.93	53.0	Unknown		Insoluble
	Se	3.32	29.2	Unknown		Insoluble
	Ti	2.93	14.0	Unknown		–
	V	2.69	4.7	Unknown		–
	Cr	2.57	–			–
	Mn	2.60	1.2	60	58.68	–
	Fe	2.54	1.2	Unlimited		–
	Co	2.50	2.7	41.0	38.01	–
	Ni	2.49	3.1	35	32.80	–
	Cu	2.55	0.8	Insoluble		–
	Zn	2.748	6.9	Unknown		Insoluble
	Ga	2.74	6.6	Unknown		Insoluble
	Cl	2.78	8.2	Unknown		Insoluble
V	As	2.80	8.9	Unknown		Insoluble
	Rb	5.4	110.0	Unknown		Insoluble
	Sr	4.29	67.0	Unknown		Insoluble
	V	3.62	40.8	Unknown		Insoluble
	Zr	3.19	24.2	Unknown		Very limited solubility
	Nb	2.94	14.4	Limited		–
	Mo	2.80	8.9	Unlimited		–
	Te	–	–	–		–
	Ru	2.66	3.5	Unknown		Limited solubility
	Rh	2.667	4.4	Unknown		Limited solubility
	Pd	2.745	6.8	10	5.14	–
	Ag	2.883	12.2	Does not mix		–
	Cd	3.042	18.4	Does not mix		–
	Zn	3.138	22.0	Unknown		Insoluble
	Sn	3.168	23.2	Does not mix		Insoluble
	Sb	3.228	25.6	12	5.5	–
VI	Cs	5.40	110	Unknown		Insoluble
	Ba	4.48	74.4	Unknown		Insoluble
	La	3.64	41.7	Unknown		Insoluble
	Hf	3.17	23.4	Unknown		Very limited solubility
	Ta	2.94	14.4	Limited		–
	W	2.82	9.7	Unlimited		–

TABLE 1 (continuation)

1	2	3	4	5	6	7
	Re	2.75	7.0	Unknown		Limited solubility
	Os	2.70	5.1	Unknown		Limited solubility
	Ir	2.709	5.4	Unknown		Limited solubility
	Pt	1.769	7.8	–		Limited solubility
	Au	2.877	11.9	10		–
	Hg	3.10	20.4	Does not mix		–
	Tl	3.427	33.4	Unknown		Insoluble
	Pb	3.494	36.0	Does not mix		–
	Bi	3.64	41.7	Does not mix		–
VII	Ra	—	—	—		–
	Th	3.60	40.0	Unknown		Insoluble
	U	2.81	9.3	Unknown		Limited solbuility

In the case of beryllium, more favorable conditions exist for the formation of solid solutions with chromium. The difference in atomic diameter between beryllium and chromium is only 12.4%, and this circumstance favors the dissolution of beryllium in chromium. According to recent data from the literature [9], beryllium will alloy with chromium and forms solid solutions of high concentration.

The remaining elements of Period II—B, C, N, and O—show an ever increasing difference in diameter (from that of chromium). As will be seen from Table 1, the atomic diameters diminish from boron to oxygen. Accordingly, the solubility of these elements in chromium, if they have any, will fall progressively in this series of elements. Although there are no data in the literature in this case, we must nevertheless suppose that these elements fall into the following order with respect to solubility: B > C > N > O.

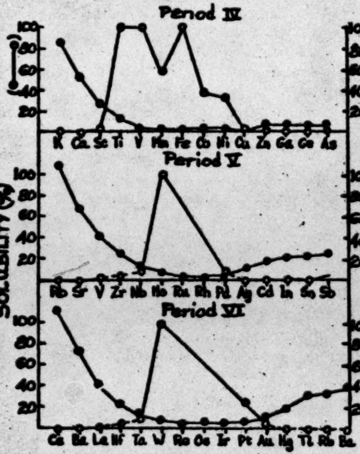
The sharp fall in the ability of chromium to form solid solutions with carbon, nitrogen, and oxygen explains the highly deleterious effect of these elements on the properties of chromium. When they are present in an insignificant concentration in chromium, the chromium carbides, nitrides, and oxides formed in hundredths or thousandths of one percent greatly impair the mechanical properties of the chromium, and increase its hardness and brittleness [10]. The deleterious effects of hydrogen, carbon, nitrogen, and oxygen on the properties of chromium are convincingly demonstrated in the papers [10] and [11]. It may be considered, therefore, on the basis of atomic diameter relationships, that only beryllium and boron are able to yield solid solutions with chromium, beryllium being able to dissolve in chromium to the extent of 9%, and boron, possibly, to the extent of tenths or hundredths of one percent.

Elements of Period III, Na, Mg, Al, Si, P, and S, depending on their positions in Mendeleev's system of elements and on the differences of their properties from those of chromium, behave differently. Sodium and magnesium, the elements furthest removed from chromium and having atomic diameter differences of 49.0% and 24.5%, respectively, do not interact with chromium: they form neither liquid nor solid solutions with it. Other elements analogous to magnesium behave similarly toward chromium. Also calcium, strontium, and barium — the remaining elements of the alkaline earth group — do not interact with chromium. The higher affinity of metals of this group for oxygen and halogens, as compared to the affinity of chromium, and their complete insolubility in chromium in the molten or solid state make it possible to apply some of the alkaline earth metals, e.g. magnesium and calcium, in a displacement reaction that leads to the preparation of pure chromium. This is the basis of the method of preparing very pure chromium by the reduction of chromic chloride with metallic calcium or magnesium [11].

Of the elements following in this period, aluminum and silicon have diameters that are closer to that of chromium, the differences being 8.9% in each case. Both elements accordingly have apprecible solubility in chromium (Table 1). The formation of unlimited solid solutions between chromium and silicon is excluded, in spite of the favorable diameter relation, because of the differences in the atomic and crystalline structures of chromium and the metalloid silicon. Aluminum and silicon, which form limited solid solutions with chromium, are of value for the improvement of the properties of metallic chromium: they find application as components of chromium alloys [12]. The two succeeding elements, phosphorus and sulfur, which differ from chromium appreciably (14.4% and 20%) in atomic diameter, should not yield solid solutions of appreciable concentration with chromium. Although there are no data in the literature on the solubility of phosphorus and sulfur in chromium in the solid state, it may be asserted that the solubility of phosphorus, if determined, will be not more than some tenths of one percent, while that of sulfur, of course, will be still less Phosphorus and sulfur, being elements of low solubility in chromium, have a deleterious effect on the properties of metallic chromium. This effect of sulfur and phosphorus on chromium is analogous to the similar deleterious effect of these elements on the properties of iron and nickel.

The atomic diameter differences with respect to chromium, and the solubilities in chromium, are shown for the elements of the long periods IV, V, and VI in the figure below. An examination of the relationships between these curves permits us to make interesting inferences concerning the dependence of the chrome-solubility of the elements on their positions in these periods. We shall examine the elements of the even and odd rows of these periods separately. As stated above, all the alkali and alkaline earth metals of these periods fail to interact with chromium and do not form either liquid or solid solutions with it.

On the basis of atomic diameter relationships, it may be supposed that chromium will also fail to give solid solutions with scandium, yttrium, and lanthanum. As we pass, however, to the metals of Groups IV, V, VI, VII, and VIII of the even rows of these periods, the atomic diameters become closer to that of chromium, thus favoring formation of chromium alloys with these metals. For example, the elements of Period IV, Ti, V, Mn, Fe, Co, and Ni, are in the same row as chromium. They differ little from chromium in atomic diameter, and they form solid solutions with chromium. Titanium, in the high-temperature modification that is isomorphous with chromium (space-centered lattice), forms unlimited solid solutions with chromium at high temperatures [13], even though there is a difference in atomic diameter of 14% under room temperature conditions. This may be explained as follows. As we have shown [14], owing to their differing coefficients of expansion, the relations between the atomic diameters of metals change at high temperatures. In the case of chromium and titanium, for which α has the values 8.1×10^{-6} and 7.2×10^{-6} cm respectively, it may be supposed that, owing to the differing coefficients of expansion, the difference in atomic diameter will be reduced. This is the explanation of the unlimited solid solutions formed by chromium and the high-temperature β-modification of titanium [13].



On the basis of the above-stated rules for the formation of unlimited solid solutions, it may be asserted that chromium must form unlimited solid solutions with vanadium and iron (α-modification), since these have similar atomic diameters and isomorphous crystal structure. There are no exact data in the literature on vanadium, but it is known that at high temperatures chromium gives unlimited solid solutions with α-Fe. The possibility indicated by the similarity in atomic diameters of the formation of unlimited solid solutions of chromium with manganese, cobalt, and nickel is not realized owing to their nonisomorphous crystalline structures and the existence of various modifications of manganese and cobalt. For this reason these three metals form only limited solid solutions with chromium (Table 1 and figure).

The elements of the remaining two even rows (6 and 8) of these periods behave analogously to the elements of the fourth row with respect to chromium. This analogy is readily revealed by comparing the solubilities in chromium of the metals of corresponding groups, taking into account the differences in atomic diameter. Thus, the metals of Group IV, i.e., the titanium analogs zirconium, hafnium, and thorium, show, unlike titanium, a growing difference in atomic diameters (24.2, 23.4, and 40.0 respectively). This is bound to lead to the inability of these metals to form solid solutions with chromium. Although there are no data in the literature regarding the solubilities of zirconium, hafnium, and thorium in chromium, it must be supposed that these solubilities are either insignificant (Zr and Hf), or absolutely zero (Th).

From the atomic diameter relationship we may predict also the existence of only limited solid solutions in chromium of the Group V metals niobium and tantalum. Having a difference in atomic diameter of only 4.7%, V and Cr, as stated above, can form unlimited solid solutions, but the vanadium analogs niobium and tantalum, which differ in atomic diameter from chromium by 14.4%, can form only limited solid solutions. A different position is found for the chromium analogs molybdenum and tungsten. They occur in the chromium group and have differences in atomic diameter of 8.9% and 9.7% respectively. On the basis of these data we suggested already in 1948, when examining multicomponent solid solutions of iron with chromium, molybdenum, and other metals [15], that it was possible for molybdenum and tungsten to form unlimited solid solutions with chromium. This suggestion was made in spite of the data then existing in the literature [16] concerning the formation of eutectic mixtures of chromium with molybdenum and tungsten. In experimental investigations that appeared at that time our suppositions received confirmation [17]. The question of the formation of unlimited solid solutions of chromium with molybdenum and tungsten has now been unequivocally solved. Owing to the somewhat greater difference in atomic diameter between chromium and tungsten that exists at low (room) temperature, the unlimited solid solutions formed by these metals are stable only at high temperatures, at which, of course, we may form an idea of the reduction in this difference from the relation between the coefficients of linear expansion [14]. It has been established experimentally that, on being cooled, the unlimited solid solutions of chromium in tungsten separate into two solid solutions. There is no information in the literature relating to the solubility of uranium in chromium. On the basis of the small difference in atomic diameter (9.6%) and the occurrence of the metals in the same group, it may be predicted that they will be found to form limited solid solutions. Formation of unlimited solid solutions is excluded in this system because of the nonisomorphous structure of uranium and its various modifications.

TABLE 2
Binary Chromium Systems

No.	System	No.	System	No.	System
	Unlimited solid solutions	4	Cr – Si	17	Cr – Ir; Cr – Pt
1	Cr – Ti (β)	5	Cr – Mn	18	Cr – Au
2	Cr – V	6	Cr – Co	19	Cr – U and others.
3	Cr – Fe (α)	7	Cr – Ni	20	Two immiscible layers: systems containing metals of the alkali and alkaline earth groups (with the exception of beryllium and some elements of Subgroup B (Pb, Bi))
4	Cr – Mo	8	Cr – Zr		
5	Cr – W	9	Cr – Nb		
	Limited solid solutions	10	Cr – Ru		
1	Cr – Be	11	Cr – Rh		
2	Cr – B	12	Cr – Pd		
3	Cr – Al	13	Cr – Hf		
		14	Cr – Ta		
		15	Cr – Re		
		16	Cr – Os		

As regards the remaining elements of the even rows of the long periods – Ru, Rh, Pd; Os, Ir, Pt – in spite of the closeness in atomic diameter, they cannot give unlimited solid solutions with chromium owing to their nonisomorphous crystal structures. They will all form only limited solid solutions with chromium. The data in the literature relating to the interaction of palladium and platinum with chromium [18, 19] confirm the possibility of forming only limited solid solutions with these metals. With regard to the other elements (Ru, Rh; Os, Ir), although there are no data in the literature, limited solubility in chromium may again be predicted.

As regards the solubilities of elements of the odd rows of Periods IV, V, and VI (or Subgroup B of the periodic system), it must be stated that, like their solubilities in iron and nickel [2, 3], these do not fully conform to the rules derived for the solubilities of elements of a given subgroup, particularly metals of Subgroup A. The data in the literature enable us to state that the elements Cu, Zn, Ga; Ag, Cd; In, Au, Hg, Tl, Pl, Bi and Po, in accordance with their positions in the period system (the most far removed from chromium) are, with the exception of gold, unable to give solid solutions with chromium. Many of them do not mix with chromium even in the liquid state (Pb, Bi, and others), but form two layers. The chromium-gold system gives mutually limited solutions, yielding a phase diagram of the peritectic type.

The elements that are nearer to chromium (Ge, As, Sn, Sb) are able to interact with it and form limited solid solutions and compounds having bonds of the metallic type. There are indications in the literature [16] that Sn and Sb have limited solubility in chromium. The existence of limited solid solutions may be postulated for Ge and As, as analogs of Sn and Sb having even lower atomic diameter differences from chromium.

After an examination, therefore, of the solubilities of the great majority of the elements in chromium, we may present a classification of chromium solid solutions as binary systems. In Table 2 data are given on binary metal systems containing chromium, which are classified as unlimited solid solutions, limited solid solutions , and systems in which two immiscible layers are formed.

As will be seen from Table 2, there are only five binary systems containing chromium that form unlimited solid solutions, and four of these have been studied experimentally; more than twenty systems form limited solid solutions, and most of these have not been studied.

SUMMARY

1. An examination of the solubilities of elements in chromium reveals regularities that are analogous to those that characterize the solubility of elements in other metals, such as iron, nickel, and copper.

2. The formation or nonformation of solid solutions of elements in chromium is determined by the relative similarity or dissimilarity of the chemical properties of the elements, as revealed by Mendeleev's periodic law.

3. On the basis of these concepts it is possible to predict the ability or inability of the elements of the periodic system to form solid solutions with chromium.

4. It is possible either to confirm the conclusions derived from crystallographic laws for the formation of metallic solid solutions by reference to information available in the literature on the solubility of one or other element in chromium or, on the other hand, to predict the ability or inability of chromium to form solid solutions in systems not yet studied experimentally.

5. It may be asserted that chromium forms unlimited solid solutions with titanium (in its high-temperature β-modification), vanadium, molybdenum, and tungsten, but only limited solid solutions with beryllium, boron, zirconium, hafnium, uranium, rhenium, and all metals of Group VIII (the iron and platinum group) with the exception of α-Fe, which has a structure isomorphous with that of chromium; with the last, chromium forms unlimited solid solutions.

6. Neither the metals furthest removed from chromium — the alkali and alkaline earth metals of Groups I and II (with the exception of beryllium) — nor those which are most different from chromium with respect to atomic diameter can form solutions with chromium, either in the solid or in the liquid state.

7. Examination of the solubility of elements of the periodic system in chromium in binary systems permits us to extend these conclusions in order to predict the ability or inability for chromium to form more complex solid solutions in ternary, quaternary, and more complicated systems.

8. Data on the solubility of elements in chromium in binary, ternary, and more complicated systems permit us to determine the possibility of preparing chromium alloys of simple or complex composition, corresponding to regions of unlimited or limited solid solutions of chromium.

9. The regularities established with respect to the solubility of the elements in chromium permit us to examine the question of the formation of solid solutions based on chromium analogs — molybdenum and tungsten. Certain regularities that have been demonstrated for chromium should be found valid also for the solubility of elements of the periodic system in molybdenum and tungsten.

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SPLITTING OF HYDROGEN CHLORIDE FROM $\alpha,\alpha,\alpha,\omega$-TETRACHLOROALKANES AND α,α,α-TRICHLOROALKANES

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Halogen derivatives of hydrocarbons of the types $Cl(CH_2CH_2)_nCCl_3$ and $H(CH_2CH_2)_nCCl_3$ have become readily accessible by the telomerization reaction of ethylene with carbon tetrachloride and chloroform respectively [1]. Comparatively little study has been devoted to the reactivities of these compounds. Among the possible changes that they may undergo, an important place must be assigned to reactions involving removal of the elements of hydrogen chloride as a means of passing to unsaturated polyhalo derivatives. By the removal of the elements of hydrogen chloride from 1,1,1,3-tetrachlorpropane with alcoholic alkali, two substances have been obtained, 3,3,3-trichloropropene and 1,1,3-trichloropropene, which were readily separated by distillation [2].

The removal of elements of hydrogen chloride from higher tetrachloroalkanes containing trichloromethyl groups has been described only in patents [3]. It is there indicated that the splitting off of hydrogen chloride catalytically and by alkaline agents involves only the chlorine of the trichloromethyl group, giving trichloroalkenes of the structure $CCl_2 = CH-(CH_2CH_2)_nCH_2Cl$. We have found that, when the reaction is effected with alcoholic alkali, it does not proceed in one direction only: we obtained a mixture of products having close boiling points that were difficult to separate. It should be noted that constants given in the patents for the compounds obtained by removal of hydrogen chloride, e.g. 1,1,5-trichloropentene, have been found to be inaccurate, as is evident from the great discrepancy between the found and calculated values of molecular refraction. We considered that it would be of great interest to apply catalytic methods for the removal of elements of hydrogen chloride from these polyhalo derivatives. There are a number of examples in the literature of removal of hydrogen chloride from polyhalo derivatives in presence of aluminum chloride; thus, we have the preparation of hexachloropropene from heptachloropropane [4], the preparation of tetrachloroethylene from pentachloroethane [5], and other examples [6]. In all these cases the reaction was carried out at a comparatively high temperature, which limited the field of application of the method. Cases are known of the removal of hydrogen chloride by heating with anhydrous ferric chloride, for example, that of DDT [7], which was also carried out at a comparatively high temperature.

We have found that hydrogen chloride is readily split from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and α,α,α-trichloroalkanes in presence of small amounts of aluminum chloride or, particularly, anhydrous ferric chloride. Reaction begins at room temperature, and for its completion a short time at 40-60° is required; dichlorovinyl derivatives, $ClCH_2(CH_2CH_2)_nCH = CCl_2$ and $CH_3(CH_2CH_2)_nCH = CCl_2$ are obtained in good yield. Under these conditions no by-products are formed and isomerization of the paraffin chain does not occur. The reaction is general for polyhalo derivatives of the structures indicated: we have by this method removed elements of hydrogen chloride from 1,1,1,5-tetrachloropentane, 1,1,1,7-tetrachloroheptane, 1,1,1,9-tetrachlorononane, 1,1,1-trichloropropane, 1,1,1-trichloropentane, and 1,1,1-trichloroheptane.

EXPERIMENTAL

1,1,5-Trichloropentene

a) 1,1,1,5-Tetrachloropentane (210 g) was heated with anhydrous ferric chloride (3 g) at 45-55° for 2 hours 30 minutes. During this time 32.6 g of hydrogen chloride was evolved. The reaction mixture was poured into water in order to dissolve the ferric chloride. The product obtained was then washed with a 10% solution of caustic soda and dried over calcium chloride. Vacuum fractionation through a 40-cm column yielded 151 g (87%) of trichloropentene and 24 g of unchanged tetrachloropentane.

b) Tetrachloropentane (42 g) and aluminum chloride (0.5 g) were heated together at 35-45° for 40 minutes; 7 g of hydrogen chloride was evolved. Aluminum chloride was removed by careful washing with water and then 10% caustic soda, and the product was dried over calcium chloride. Vacuum fractionation yielded 26 g (77%) of trichloropentene and 4.2 g of unchanged tetrachloropentane. The 1,1,5-trichloropentene had b.p. 68-69°/7 mm, n_D^{20} 1.4892; d_4^{20} 1.2724; found MR 39.37; calculated MR 39.42. The literature [3] gives n_D^{25} 1.4878; d_4^{25} 1.2893, found MR 38.76.

Found %: C 34.42; 34.45; H 4.07; 4.10

$C_5H_7Cl_3$. Calculated %: C 34.57; H 4.03

Hydrolysis of the trichloropentene with concentrated sulfuric acid gave a 92% yield of 5-chlorovaleric acid. From this, via the acid chloride, the amide of 5-chlorovaleric acid, m.p. 78-79°, was prepared. In admixture with authentic amide it melted at 78-79°. The trichloropentene obtained therefore contained a normal chain.

1,1,7-Trichloroheptene

A mixture of 108 g of tetrachloroheptane and 2 g of anhydrous ferric chloride was heated for three hours at 45-55°; 15.2 g of hydrogen chloride was evolved. Vacuum fractionation yielded 76.1 g (73%) of trichloroheptene and 8 g of unchanged tetrachloroheptane. 1,1,7-Trichloroheptene had b.p. 66-67°/ 1 mm or 101-102°/ 8mm; n_D^{20} 1.4850; d_4^{20} 1.1902; found MR 48.52; calculated MR 48.66. The literature [3] gives n_D^{20} 1.4850.

Found %: C 41.52; 41.58; H 5.40; 5.56

$C_7H_{11}Cl_3$. Calculated %: C 41.68; H 5.45

1,1,9-Trichlorononene

Tetrachlorononane (50 g) and anhydrous ferric chloride (1.5 g) at 45-55° for three hours yielded 31.6 g (73%) of trichlorononene and 8 g of unchanged tetrachlorononane. 1,1,9-trichlorononene had b.p. 91-92°/ 1.5 mm, n_D^{20} 1.4834; d_4^{20} 1.1342; found MR 57.83; calculated MR 57.90.

Hydrolysis of the trichlorononene yielded 9-chlorononanoic acid, from which, via the acid chloride, the amide, m.p. 76-77°, was prepared. In admixture with authentic amide it melted at 76-77°. The trichlorononene therefore contained a normal carbon chain.

1,1-Dichloropropene

1,1-Dichloropropene was prepared in 85% yield; b.p. 77-78°; n_D^{20} 1.4450; d_4^{20} 1.1687.

1,1-Dichloropentene

From 74 g of trichloropentane and 1.5 g of anhydrous ferric chloride at 40-50° for three hours, 46.2 g (81%) of dichloropentene and 5.1 g of unchanged trichloropentane were obtained. 1,1-Dichloropentene had b.p. 127-128°; n_D^{20} 1.4548; d_4^{20} 1.0899; found MR 34.59; calculated MR 34.55.

Found %: C 43.17; 42.98; H 5.93; 5.86.

$C_5H_8Cl_2$. Calculated %: C 43.16; H 5.75

Hydrolysis of the dichloropentene with concentrated sulfuric acid yielded valeric acid, from which, via the acid chloride, the anilide, m.p. 62.5-63°, was prepared. In admixture with authentic valeranilide, it melted at 62.5-63°.

1,1-Dichloroheptene

1,1-Dichloroheptene was prepared from trichloroheptane and anhydrous ferric chloride in 80% yield. 1,1-Dichloroheptene had b.p. 68-69°/14 mm; n_D^{20} 1.4589; d_4^{20} 1.0430; found MR 43.76; calculated MR 43.79.

Found %: C 50.05; 50.04; H 7.26; 7.22

$C_7H_{12}Cl_2$. Calculated %: C 50.29; H 7.18.

Hydrolysis of the dichloroheptene with concentrated sulfuric acid yielded heptanoic acid, from which the anilide, m.p. 64-65°, was prepared via the acid chloride. The mixed melting point test gave 64-65°.

SUMMARY

1. A method has been proposed for the splitting of hydrogen chloride from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and α,α,α-trichloroalkanes by heating these substances with catalytic amounts of anhydrous ferric chloride.

2. It has been shown that no isomerization of the carbon chain occurs under the conditions used for the removal of the elements of hydrogen chloride in presence of anhydrous ferric chloride or aluminum chloride.

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2-AMINOVINYL KETONES

COMMUNICATION 1. SYNTHESIS OF ALKYL 2-DIALKYLAMINOVINYL KETONES

N. K. Kochetkov

Alkyl 2-dialkylaminovinyl ketones $RCOCH = CHNR'_2$ belong to a very interesting, but little studied, class of so-called "enamine" compounds. They are among the simplest members of this class, and they exhibit very clearly the characteristic features of the chemical behavior of enamine compounds. 2-Dialkylaminovinyl ketones may be prepared by the reaction of 2-hydroxyvinyl ketones with secondary amines, but this method finds its main application in the preparation of compounds of complex structure [1, 2]. Also, 2-dialkylaminovinyl ketones have been prepared by the addition of amines to ketones containing a triple bond [3, 4]. This method of synthesis can scarcely be regarded as convenient from the preparative point of view owing to the low accessibility of the starting materials. Owing to the fact that the simplest members of this class of compounds are relatively inaccessible, their chemical behavior has not been studied in sufficient detail, in spite of the interest that they undoubtedly present.

Continuing our investigations of the chemical reactions of alkyl 2-chlorovinyl ketones, we have made a detailed study of the reactions of these with amines with the object of developing a convenient synthesis of N-substituted 2-aminovinyl ketones. There are indications in the patent literature [5] that alkyl 2-chlorovinyl ketones react with amines with formation of 2-aminovinyl ketones, and it is recommended that this reaction be performed in an organic solvent. Numerous repeats of the synthesis under various conditions showed that 2-aminovinyl ketones were indeed formed, but in yields not exceeding 15-25%. Further work in this direction enabled us to simplify and greatly improve this reaction. It was found that the reaction of alkyl 2-chlorovinyl ketones proceeds most smoothly in aqueous medium, and this fact made it possible for us to develop a very simple and convenient method for the synthesis of alkyl 2-dialkylaminovinyl ketones in yields of 60-85%. The best results were obtained in the reaction when the 2-chlorovinyl ketone was added gradually to an aqueous solution of the amine, taken in a quantity of rather more than two moles per mole of 2-chlorovinyl ketone; the reaction then went very vigorously and was not accompanied by any appreciable side reactions:

$$RCOCH = CHCl + 2NHR'_2 \rightarrow RCOCH = CHNR'_2 + NHR_2 \cdot HCl.$$

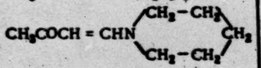
The amine concentration is of considerable importance: it is most convenient to use an aqueous solution of about 50% strength, the yield being appreciably reduced when more dilute solutions are employed.

The method we have developed for the synthesis of N-substituted alkyl 2-aminovinyl ketones makes it possible to obtain considerable quantities of these substances in a very short time and renders them readily available for further study and application. By this method we have obtained several previously unknown alkyl 2-dialkylaminovinyl ketones, and the yield and constants of these are given in the table.

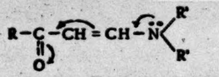
All the compounds prepared are yellowish oily liquids that can be preserved for a long time without change. They are miscible in all proportions with water and with most organic solvents. The physical constants of the substances obtained are given in the table. First of all, the anomalously high boiling points of alkyl 2-dialkylaminovinyl ketones attract attention: they are 60-70° higher than those of their saturated isologs. For example, 4-dimethylamino-2-butanone boils at 57-58°/18 mm; i.e., about 70° below the b.p. of the alkyl 2-dialkylaminovinyl ketone of analogous structure, 4-dimethylamino-3-buten-2-one. All the compounds prepared show also a very high exaltation of molecular refraction (4-5 units).

TABLE

Properties of Alkyl 2-Dialkylaminovinyl Ketones

Formula	Yield (%)	B.p. (°C, p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	EMR
$CH_3COCH = CHN(CH_3)_2$	76.5	101-102 (5)	1.5562	0.9734	37.38	33.40	3.98
$CH_3COCH = CHN(C_2H_5)_2$	83.5	124-125 (6)	1.5378	0.9344	47.26	43.63	4.63
	70.0	154-155 (7)	1.5730	1.0103	49.97	45.05	4.92
$n\text{-}C_3H_7COCH = CHN(CH_3)_2$	61.0	120-121 (5)	1.5364	0.9339	47.18	42.63	4.55
$i\text{-}C_4H_9COCH = CHN(CH_3)_2$	66.0	124-125 (4)	1.5270	0.9245	51.61	47.25	4.36

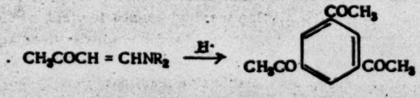
Already on the basis of the physical properties (solubility, high boiling point), we may infer the presence of considerable polarity in alkyl 2-dialkylaminovinyl ketone molecules resulting from interaction between the carbonyl group and the free electron pair on the nitrogen:



This suggestion is well confirmed by results obtained for the dipole moments of these compounds, which have been determined by A. N. Shidlovskaya. Other investigators [4] have come to a similar conclusion on the basis of adsorption spectra studies.

The chemical properties of alkyl 2-dialkylaminovinyl ketones are in accord with this hypothesis. The above scheme, in which the carbonyl group is conjugated with the electron pair of the nitrogen atom, is bound to result in a reduction in basic character and in the suppression of the activities both of the double bond and of the carbonyl group.

Actually, alkyl 2-dialkylaminovinyl ketones have practically no basic properties. Under the action of acids they are rapidly hydrolyzed at the nitrogen-carbon bond. Thus, even a very short treatment with warm acetic acid brings about the decomposition of 4-dimethylamino-3-buten-2-one, a quantitative yield of 1,3,5-triacetylbenzene being obtained; mineral acids react in similar fashion even in the cold:



Alkyl 2-dialkylaminovinyl ketones form picrates, but these are comparatively unstable, and are partially destroyed during recrystallization. The suppression of basic properties and the lability of the C – N bond are manifestations of the operation of a well-known principle of vinylogy. Alkyl 2-dialkylaminovinyl ketones are vinylogs of dialkylamides of acids, and their behavior corresponds to the behavior of amides.

EXPERIMENTAL

I. 4-Dimethylamino-3-buten-2-one

4-Chloro-3-buten-2-one (16.0 g) was added gradually to 70 ml of a 40% aqueous solution of dimethylamine with vigorous stirring and application of cooling in an ice-salt mixture. The reaction was very vigorous and was accompanied by considerable evolution of heat. The homogeneous reaction mixture was stirred for 30 minutes at room temperature, and was then saturated with potassium carbonate and extracted with ether in a liquid extractor for 12 hours. The ether extract was dried over calcined potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled, when it all came over at 131-133°/20 mm, the yield being 13.5 g (76.5%). After redistillation 4-dimethylamino-3 buten-2-one had the following constants:

b.p. 101-102° (5 mm); d_4^{20} 0.9734; n_D^{20} 1.5562; found MR 37.38; calculated for $C_6H_{11}ON\,\overline{F}$ MR 33.40; EMR 3.98.

	Found %:	N 12.24; 12.40
$C_6H_{11}ON$.	Calculated %:	N 12.37

4-Dimethylamino-3-buten-2-one is a yellowish oil having a feeble odor reminiscent of amides. It may be preserved for a long time without change. It mixes in all proportions with water and organic solvents. It gives a cherry-red color with ferric chloride.

The picrate was prepared in ether; m.p. after careful recrystallization from alcohol: 116-118°.

	Found %:	N 16.47; 16.38
$C_{12}H_{14}O_8N_4$	Calculated %:	N 16.31

II. 4-Diethylamino-3-buten-2-one

4-Diethylamino-3-buten-2-one was prepared in similar manner to the preceding substance from a solution of 85 g of diethylamine in 90 ml of water and 58.0 g of 4-chloro-3-buten-2-one. The yield was 66.0 g (83.5%). After redistillation 4-diethylamino-3-buten-2-one had the following constants: b.p. 124-125° (6 mm); d_4^{20} 0.9344; n_D^{20} 1.5378; found MR 47.26; calculated for $C_8H_{15}ON\,\overline{F}$ MR 46.63; EMR 4.63.

	Found %:	C 67.84; 67.91;	H 10.77; 10.86;	N 10.51; 10.59
$C_8H_{15}ON$.	Calculated %:	C 68.04;	H 10.70;	N 9.91

4-Diethylamino-3-buten-2-one is a yellowish oil of feeble odor, stable to storage. It dissolves in water and organic solvents. It gives a cherry-red color with ferric chloride.

The picrate was prepared in absolute alcohol and recrystallized from the same solvent: fine yellow crystals, m.p. 115-116°

	Found %:	N 15.09; 15.21
$C_{14}H_{18}O_8N_4$	Calculated %:	N 15.12

III. 4-Piperidino-3-buten-2-one

The substance was prepared according to the method of Experiment I from a solution of 38 g of piperidine in 40 ml of water and 21.0 g of 4-chloro-3-buten-2-one, the yield being 22.0 g (70%). After redistillation 4-piperidino-3-buten-2-one had the following constants: b.p. 154-155°/7 mm; d_4^{20} 1.0103; n_D^{20} 1.5730; found MR 49.97; calculated for $C_9H_{15}ON\,\overline{F}$ MR 45.05; EMR 4.92.

	Found %:	N 9.17; 8.92
$C_9H_{15}ON$.	Calculated %:	N 9.16

4-Piperidino-3-buten-2-one is a thick oil, which does not crystallize after a long freezing treatment dissolves in water and organic solvents, and gives a cherry-red color with ferric chloride.

The picrate was prepared in absolute alcohol and recrystallized from the same solvent: large yellow crystals, m.p. 122-123°.

	Found %:	N 14.73; 14.76
$C_{15}H_{18}O_8N_4$	Calculated %:	N 14.66

IV. 1-Dimethylamino-1-hexen-3-one

1-Dimethylamino-1-hexen-3-one was prepared according to the method of Experiment I from 50 ml of a 40% aqueous solution of dimethylamine and 23.0 g of 1-chloro-1-hexen-3-one, the yield being 15.0 (61%). After redistillation 1-dimethylamino-1-hexen-3-one had the following constants: b.p. 120-121°/5 mm; d_4^{20} 0.9339; n_D^{20} 1.5364; found MR 47.18; calculated for $C_8H_{15}ON\,\overline{F}$ MR 42.63; EMR 4.55.

	Found %:	N 10.03; 9.98
$C_8H_{17}ON$.	Calculated %:	N 9.91

1-Dimethylamino-1-hexen-3-one is a yellowish oil of feeble odor, which does not change with storage, mixes with water and organic solvents, and gives a cherry-red color with ferric chloride.

V. 1-Dimethylamino-5-methyl-1-hexen-3-one

1-Dimethylamino-5-methyl-1-hexen-3-one was prepared according to the method of Experiment I from 50 ml of a 40% aqueous solution of dimethylamine and 20.5 g of 1-chloro-5-methyl-1-hexen-3-one, the yield being 14.5 g (66%). After redistillation 1-dimethylamino-5-methyl-1-hexene-3-one had the following constants:

b.p. 124-125° (4 mm); d_4^{20} 0.9245; n_D^{20} 1.5270; found MR 51.61; calculated for $C_9H_{17}ON^{F}$ MR 47.25; EMR 4.36.

Found %: N 9.42; 9.44
$C_9H_{17}ON$. Calculated %: N 9.22

1-Dimethylamino-5-methyl-1-hexene-3-one is a yellowish oil of feeble odor, soluble in water and organic solvents and giving a cherry-red color with ferric chloride.

VI. Reaction of 4-Dimethylamino-3-buten-2-one with Acetic Acid

4-Dimethylamino-3-buten-2-one (5.0 g) was heated at the boil in 10 ml of aqueous acetic acid for 20 minutes. The precipitate that formed on cooling was filtered off and recrystallized from water; it consisted of colorless needles (2.8 g, 94%), m.p. 162-163°. In admixture with 1,3,5-triacetylbenzene it showed no depression of melting point. Data in the literature for triacetylbenzene: m.p. 162-162.5° [6]; m.p. 163° [7].

SUMMARY

1. By reaction of alkyl 2-chlorovinyl ketones with secondary amines in aqueous medium, alkyl 2-dialkylaminovinyl ketones are formed in 60-85% yield. This reaction appears to be the most convenient method for the preparation of compounds of this type.

2. On the basis of an examination of the physical properties of the compounds obtained, it is concluded that their molecules have considerable polarity.

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CONDENSATION OF MESO-HALO DERIVATIVES OF 1,3-DIOXO COMPOUNDS WITH UREA

L. Sekeresh and G. Fodor

Halogen derivatives of monooxo compounds are well known starting materials for the synthesis of azoles. With amides of thiocarbonic acids [1] and with thiourea [1, 2] they give thiazole derivatives, and with carbonic acid amides they give oxazole derivatives [3]. It is interesting, however, to note that condensation with urea yields imidazole derivatives, and not an aminooxazole as might be expected.

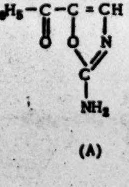
The behavior of meso-halo 1,3-dioxo compounds in such condensations has not been previously investigated. The only example described in the literature is the condensation of 3-bromo-2,4-pentanedione with 1-(N-acetylsulfanilyl)-2-thiourea, which resulted in the formation of 5-acetyl-2-(N^4-acetylsulfanilamido)-4-methylthiazole, although no proof is advanced in the patent [5] of the structure of this compound. It has been established also that a bromine atom in the meso position in 1,3-dioxo compounds splits off mainly in the form of a cation, yielding hypobromous acid [6, 7], and in other cases behaves as atomic bromine [8]. Owing to the causes indicated above, the usual metathetic reactions of halogen derivatives proceed here at very low rates [9]. It was for this reason that we considered it to be of interest to make a more extensive study of the reactions of compounds of this type, and as an example for study we chose benzoylbromoacetaldehyde, which has been prepared by Agarwal, Gupta, and Deshapande [10].

The solubility of this compound in alkali is evidence of the occurrence of aldo-enol tautomerism, though the fact that the compound reduces Fehling's solution points to the presence of a free aldehyde group. With hexamethylenetetramine it yields, in addition to an amorphous mass, a crystalline hydrobromide of hexamethylenetetramine, which is evidence of anionic elimination of bromine.

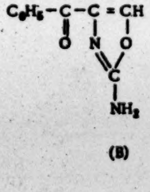
We have studied the reaction between this compound and urea. According to an empirical rule [4], which holds for α-bromo monooxo compounds, we might expect to obtain 4-benzoyl-4-imidazolin-2-one (C). On the basis, however, of the peculiar behavior of meso-halo 1,3-dioxo compounds referred to above, we must take into account the possibility of obtaining other compounds resulting from the elimination of bromine as a cation [9].

We actually found that the nitrogen compound obtained had the empirical formula $C_{10}H_8O_2N_2$ (m.p. 208-210°), and was not identical with 4-benzoyl-4-imidazolin-2-one (C) (m.p. 313°), but was an isomer of this substance. Its structure, therefore, may be represented by one of the formulas A, B, C, D, E, and F (below). Identification of the structure with one of those indicated would make it possible to obtain an idea of the reaction mechanism.

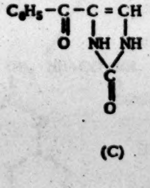
The compound obtained could not be 2-amino-5-phenyl-4-oxazolecarboxaldehyde (D) or 2-amino-4-phenyl-5-oxazolecarboxaldehyde (E), since it fails to react with dimedone. It is therefore only necessary to examine the structures A, B, and F.



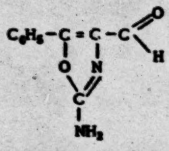
(A)



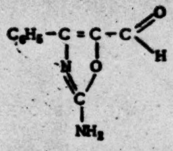
(B)



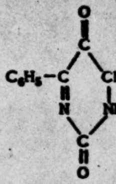
(C)



(D)

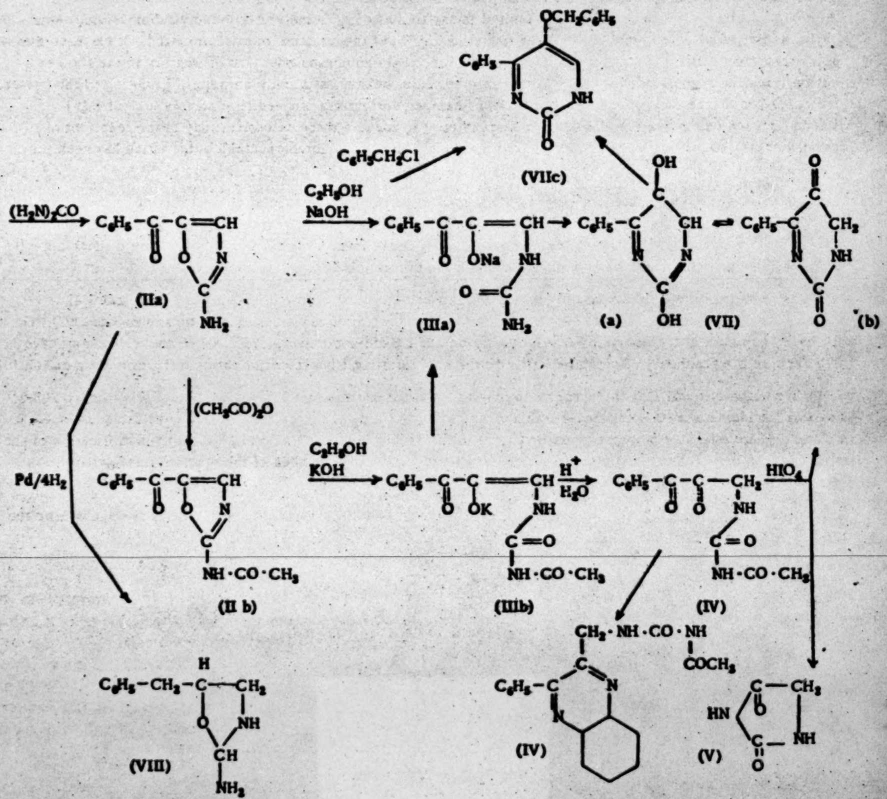


(E)



(F)

The condensation product gave a monohydrochloride and a monoacetyl derivative (IIb). By the action of caustic alkalis it was converted into a crystalline enolate, and it was found that one molecule of NaOH was taken up, so that the scission of the heterocycle must have occurred. Subsequent acidification, however, yielded not the original compound, but another, isomeric heterocycle (m.p. 320°). On the basis of a working hypothesis advanced by one of us (G. Fodor), this fact can be explained as follows: the ring of the compound first formed, i.e., 2-amino-5-benzoyloxazole (IIa), is ruptured, and the compound is converted into the Na enolate IIIa, which then, under the action of acid, forms a pyrimidine ring (see VIIa or Formula F).


(H₂N)₂CO
(IIa)
C₆H₅CH₂Cl
(VIIc)
C₂H₅OH
NaOH
(IIIa)
(a)
(VII)
(b)
(CH₃CO)₂O
Pd/4H₂
(II b)
C₂H₅OH
KOH
(IIIb)
H⁺
H₂O
HIO₄
(IV)
(VIII)
(IV)
(V)

Although the melting point of this compound is close to that of 4-benzoyl-4-imidazolin-2-one (C), its diacetyl derivative melts at 83-84°, as compared with 139°, the melting point of the diacetyl derivative of the imidazolinone; these compounds are therefore not identical. Incidentally, such high melting points are characteristic of pyrimidinol and imidazolinone derivatives.

In order to substantiate this hypothesis, we attempted to convert the supposed pyrimidine derivative by chlorination and subsequent reductive dehalogenation into the corresponding bisdesoxy compound, i.e., 4-phenylpyrimidine, which could be synthesized also by another means [12]. Chlorination, however, did not yield a homogeneous product, and the problem was therefore tackled in another way.

It was proved that the oxygen atom in the ring of the heterocyclic compound IIa (oxazole derivative) first formed corresponds to the oxygen atom of the enol group of the salt IIIa formed by the action of alkali. On treatment of the Na enolate with benzyl chloride, it was converted not into a benzyl derivative of the original compound, but into a monobenzyl ether (VIIc) of the compound $C_{10}H_8O_2N_2$ (pyrimidine derivative), which has an acid character. It was found possible to obtain this ether also by the action of benzyl chloride on the abovementioned high-melting compound (VIIa). It follows that the enol hydroxyl group does not participate in the second ring closure.

In subsequent work, therefore, we tried to prove the structure of the primary condensation product. First of all, we tried hydrogenation with the object of converting the condensation product into a known amino-1-phenylpropanediol and studying its structure. On hydrogenation in presence of palladium, however, the substance took up only four molecules of hydrogen with loss of one of its oxygen atoms, being converted into a compound of formula $C_{10}H_{14}ON_2$ (probably VIII), a compound which was very stable toward alkalis and acids; it did not enable us to draw any conclusion concerning the structure of the original compound. We therefore directed our attentions to a more thorough study not of the primary condensation product, but of its N-monoacetyl derivative (IIb). Under the action of alcoholic KOH, this monoacetyl derivative combined with one molecule of KOH, yielding a crystalline K enolate with simultaneous rupture of the heterocycle. This process was found to be reversible, IIb being re-formed on acidification. The N-acetylated product was not converted into a secondary heterocyclic compound of acidic character, but into the free base. This fact indicated that the nitrogen atom took part in the formation of the molecule of the secondary heterocyclic product, but not in the formation of the primary product IIa.

When a solution of the K enolate IIIb in 10% alcohol was treated with hydrochloric acid, and the mixture highly diluted with water, ring closure with formation of the original compound, did not occur, but the crystalline product IV separated. The 1,2-dioxo structure of this was proved as follows: 1) with o-phenylenediamine a quinoxaline derivative (VI) was obtained; 2) on being oxidized with metaperiodic acid, it broke down to give benzoic acid and hydantoin (V).

Our supposition that the structure of the compound obtained from benzoylbromoacetaldehyde and urea corresponds to Formula A, and not Formula B, was therefore confirmed. The isomeric compound obtained from it in the secondary ring closure can be only F, since the compounds C, D, and E have been altogether excluded. The diketo compound, on being warmed with hydrochloric acid is converted into the pyrimidine VII, thus proving the structure of the latter.

As a result of these proofs we may conclude that in the reaction of the meso-halo 1,3-dioxo compound studied with urea the oxygen atom of the urea molecule attacks the carbon atom linked to bromine, whereas the nitrogen atom of the imino group reacts with the carbon atom linked to the hydroxyl group of the aldo-enol system.

Such a reaction mechanism is reminiscent of that for the reaction between α-halo monooxo compounds and thiourea [2], and is not analogous to the formation of imidazolinones [4] in the reaction of α-halo monooxo compounds with urea. On the other hand, the high rate of the reaction studied is evidence in favor of the view that a halogen atom in the meso position is, contrary to expectation [9], readily eliminated in the form of an anion.

EXPERIMENTAL

Reaction of Benzoylbromoacetaldehyde with Hexamethylenetetramine. Hexamethylenetetramine (1.4 g) was dissolved in 15 ml of absolute chloroform, and benzoylbromoacetaldehyde (2.3 g) dissolved in 35 ml of absolute chloroform was added. After a few minutes, a white crystalline precipitate formed in the solution. The precipitate was filtered off, washed with chloroform, and dried, yielding 1.5 g of white crystals, m.p. 190-191°.

Delepine [13] gives the same melting point.

Found %: N 25.40; Br 36.00
$C_6H_{12}N_4HBr$. Calculated %: N 25.30; Br 36.20

The mother liquor was carefully evaporated at not above 50°, but no homogeneous compound could be obtained from the residue.

2-Amino-5-benzoyloxazole (IIa). Benzoylbromoacetaldehyde [10] (12 g; m.p. 110°) was dissolved in 250 ml of acetone, and urea (8 g) was added The reaction mixture was boiled for 40 minutes on a water bath, when all the urea dissolved. Acetone (about 200 ml) was driven off, and the remaining solution, which was of a red color, was poured with continuous stirring into water (1 liter). An oil, which solidified forming yellowish crystals (8.3 g; m.p. 180-200°), was precipitated.

Recrystallization of the crude product from ten times its weight of ethanol yielded yellowish crystals (about 50% of the crude product), m.p. 208-210°. This compound was soluble in dilute hydrochloric acid and, when warmed slightly, in 2 N NaOH.

Found %: C 63.87; H 4.19; N 15.39
$C_{10}H_8O_2N_2$. Calculated %: C 63.77; H 4.29; N 14.88

The crude product was dissolved in twice its weight of 18% hydrochloric acid on a water bath and filtered. Concentrated ammonia was then added to a weakly alkaline reaction. The product purified in this way also melted at 208-210°.

Its Hydrochloride. 2-Amino-5-benzoyloxazole (0.9 g) was heated on a water bath with 25 ml of 20% hydrochloric acid until solution was complete, and the mixture was then evaporated under reduced pressure. The residual crystalline mass was recrystallized from 10 ml of ethanol, yielding 0.25 g of the hydrochloride, m.p. 198-200°.

Found %: C 53.86; H 4.38; N 12.13; Cl 15.89
$C_{10}H_9O_2N_2Cl$. Calculated %: C 53.46; H 4.03; N 12.47; Cl 15.78

Its Acetyl Derivative (IIb). 2-Amino-5-benzoyloxazole (0.9 g) was dissolved in 5 ml of acetic anhydride, and the mixture was heated under reflux for one hour. On the next day crystals separated from the mixture; they were filtered off and washed with ethyl acetate The yield of crystals (m.p. 189-191°) was 0.55 g. The melting point of a mixture with IIa was 163°.

Found %: C 62.13; H 4.52; N 12.32
$C_{12}H_{10}O_3N_2$. Calculated %: C 62.60; H 4.37; N 12.16

The Transformations IIb → IIIb → IIb. The acetyl derivative IIb was dissolved in a hot 10% alcoholic solution of KOH, giving a solution from which a K enolate crystallized out on cooling. The solution was diluted with water and acidified to Congo red with hydrochloric acid. The crystals that separated melted at 185-188°, and in admixture with the original substance showed no depression in melting point.

Catalytic Hydrogenation of IIa and IV. a) 2-Amino-5-benzoyloxazole (IIa; 2 g) was dissolved in 100 ml of 96% ethanol and, after addition of 1 ml of a 20% solution of dry HCl in alcohol, was hydrogenated in presence of 0.5 g of palladized bone charcoal (20% Pd), 845 ml of hydrogen being absorbed in 145 minutes (4 moles of H_2 = 950 ml). The alcoholic solution was evaporated under reduced pressure, and an amorphous residue (2 g) remained which when rubbed out with 10 ml of water yielded 1.5 g of a white crystalline compound, m.p. 133-143°. Recrystallization from 40 ml of ethyl acetate yielded 0.95 g of a substance, m.p. 146-148°. According to its molecular formula this compound is either 2-amino-5-benzoyloxazolidine (VIII) or an isomer of this substance, (3-phenylpropyl)urea.

Found %: C 67.44; H 8.01; N 15.2
$C_{10}H_{14}ON_2$. Calculated %: C 67.38; H 7.92; N 15.72

b) 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IV; 2.5 g) was dissolved in 120 ml of alcohol and, after addition of 4 ml of a concentrated solution of dry HCl in alcohol, was hydrogenated in presence of 0.5 g of palladized bone charcoal (20% Pd), 750 ml of hydrogen being absorbed in 145 minutes. The colorless alcoholic solution was evaporated down, and the oil remaining was rubbed out with 50 ml of water, yielding a crystalline product (0.6 g). Recrystallization from a small amount of ethyl acetate yielded 0.4 g of a substance of m.p. 146-148°. This product showed no depression in melting point when mixed with the product of the hydrogenation of 2-amino-5-benzoyloxazole.

In order to study the structure of this hydrogenation product, experiments were made on its splitting by acids and alkalis: 1) The hydrogenation product (0.5 g) was boiled with 25 ml of 20% hydrochloric acid for nine hours, and on the next day the solution was evaporated down under reduced pressure and the residue was rubbed out with a small amount of water, yielding 0.3 g of a product of m.p. 144-146°, which showed no depression in melting point when mixed with the original substance. 2) The hydregenation product (0.5 g) was boiled with 10 ml of 20% KOH solution for three hours under reflux. The solution was cooled, and white crystals separated (0.35 g; m.p. 143-145°) which showed no depression in melting point when mixed with the original substance.

Sodium Salt of the Enolate of 1-Phenyl-3-ureido-1,2-propanedione (IIIa). 2-Amino-5-benzoyloxazole (1 g) was dissolved in warm 5% aqueous NaOH, and when the solution was cooled 0.5 g of yellow crystals separated.

Found %: N 12.27; Na 11.32

$C_{10}H_9O_3N_2Na$. Calculated %: N 12.29; Na 10.08

4-Phenyl-2,5-pyrimidinediol (VII). 2-Amino-5-benzoyloxazole (1.5 g) was dissolved under slight warming in 25 ml of 2 N KOH. The hot solution was filtered and acidified with 15 ml of concentrated hydrochloric acid, when an oil separated that immediately solidified. The yellow crystals (1.5 g) obtained decomposed at about 250°. The substance was recrystallized from 75 ml of glacial acetic acid. The product (0.7 g; dec. 320°) was readily soluble in alkalis in the celd.

Found %: C 63.48; H 4.30; N 14.39

$C_{10}H_8O_2N_2$. Calculated %: C 63.83; H 4.55; N 14.89

Its Diacetyl Derivative. 4-Phenyl-2,5-pyrimidinediol (0.5 g) was dissolved in 10 ml of warm acetic anhydride. The solution was boiled for two hours, cooled, and then poured onto 100 g of ice. The oily product that separated was recrystallized from a mixture of water and acetone (one day was required), yielding dark yellow crystals, m.p. 83-84°.

Found %: C 61.12; H 4.31; N 10.34

$C_{14}H_{12}O_4N_2$. Calculated %: C 61.78; H 4.44; N 10.29

Its Monobenzyl Ether (VIIc). Benzyl chloride (2 ml) was dissolved in 10 ml of dry commercial xylene, and the sodium salt of the enolate of 1-phenyl-3-ureido-1,2-propanedione (1.5 g), ground to a powder, was added. The suspension was boiled for eight hours and then cooled. The crystals were filtered off, repeatedly washed with benzene, and then boiled with 25 ml of water. Inorganic salts were thus removed, and a yellowish crystalline mass (1 g) remained. Recrystallization from methanol yielded 0.3 g of 4-phenyl-2,5-pyrimidinediol, which decomposed at 320° (% N found: 14.91).

From the mother solution of pyrimidine derivative, yellow crystals (0.35 g), m.p. 198-200°, separated. These, according to analysis, consisted of the monobenzyl ether of 4-phenyl-2,5-pyrimidinediol.

Found %: C 73.31; H 4.97; N 10.02

$C_{17}H_{14}O_2N_2$. Calculated %: C 73.38; H 5.07; N 10.07

This compound is insoluble in hydrochloric acid; it dissolves readily in alkalis, but is reprecipitated by hydrochloric acid.

Acid Hydrolysis of the Monobenzyl Ether. The substance VIIc (0.3 g) was boiled for five hours with 5 ml of hydrobromic acid dissolved in glacial acetic acid, and the mixture was poured into 200 ml of water The amorphous substance that separated was rubbed out with methanol, yielding a crystalline compound, m.p. 320°, which showed no depression in melting point when mixed with 4-phenyl-2,5-pyrimidinediol (VIIa).

Found %: N 14.79

Calculated %: N 14.89

Potassium Salt of the Monoenolate of 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IIIb). 2-Acetamido-5-benzoyloxazole (IIb; 2.5 g) was suspended in 20 ml of alcohol, and a solution of 0.61 g of KOH in a mixture of 1 ml of water and 5 ml of ethanol was added. At first a clear solution was obtained, and then the potassium salt was rapidly precipitated. The mixture was cooled with ice, and the substance was filtered off and washed several times. The product (1.75 g) consisted of yellow crystals of good solubility in water.

Found %: N 10.61; K 14.05

$C_{12}H_{11}O_4N_2K$. Calculated %: N 9.79; K 13.64

3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IV). A solution of 1.8 g of KOH in 3 ml of water was added to a suspension of 7.5 g of 2-acetamido-5-benzoyloxazole (IIb) in 250 ml of warm ethanol. The substance dissolved, and the solution was diluted with 2000 ml of water and acidified with 50 ml of concentrated hydrochloric acid. After several hours the diketone began to separate from the solution in the form of light crystals. After one day the crystals were filtered off and dried (3 g); they were yellowish green and melted with decomposition at 214-224°. Recrystallization from methanol yielded glistening plates, m.p. 230° (dec.).

Found %: C 58.46; H 4.46; N 11.29
$C_{12}H_{12}O_4N_2$. Calculated %: C 58.06; H 4.84; N 11.28

2-(3-Acetylureidomethyl)-3-phenylquinoxaline (VI). 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (50 mg) was dissolved in 5 ml of alcohol and 50 mg of a concentrated aqueous solution of o-phenylenediamine was added. The mixture was heated for a short time on a water bath, and white woollyneedles separated, m.p. 268-270°.

Found %: C 67.52; H 5.38; N 16.90
$C_{18}H_{16}O_2N_4$. Calculated %: C 67.50; H 5.00; N 17.50

Hydantoin (V). To a suspension of 0.5 g of 3-(3-acetylureido)-1-phenyl-1,2-propanedione (IV) in 15 ml of dioxane, a solution of 0.45 g of metaperiodic acid in 3 ml of water was added. The mixture darkened, and the suspended substance went into solution with rise in temperature. The mixture was allowed to stand for 15 minutes and then neutralized to litmus with 2 N KOH. The solid substance obtained was filtered off and rubbed out with an absolute alcoholic solution of HCl. The salt formed was filtered off, and the alcoholic mother liquor was diluted with a few milliliters of alcohol and evaporated under reduced pressure. The somewhat dark colored residue was dissolved in acetone and separated from inorganic products by filtration. The acetone filtrate was evaporated down and the residue rubbed out with a small amount of water, yielding 40 mg of a white crystalline compound of m.p. 218-221°. Lippmann [14] gives 220-221° for the melting point of hydantoin.

Found %: C 35.15; H 4.09; N 28.24
$C_3H_4O_2N_2$. Calculated %: C 36.00; H 4.00; N 28.00

The product in admixture with hydantoin prepared from hydantoic acid showed no depression in melting point.

The dioxane mother liquor was evaporated under reduced pressure, and the residual crystalline mass was dissolved successively in alcohol and in concentrated aqueous hydrochloric acid, dissolution being followed in each case by evaporation. The dark colored residue was recrystallized from 50% aqueous alcohol, and the product consisted of crystals, m.p. 118-121°, which showed no depression in melting point when mixed with benzoic acid.

* * *

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HIGH TEMPERATURE CATALYTIC DEHYDROGENATION OF ETHYLCYCLOHEXANE

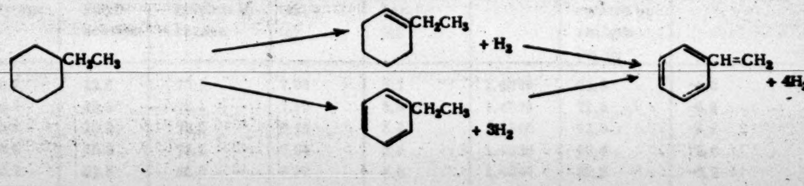
COMMUNICATION 1. MAIN DIRECTION OF THE REACTION

N. I. Shuikin and I. I. Levitsky

The dehydrogenation of cyclohexane hydrocarbons in presence of oxide catalysts was first described in the literature by Balandin and Brusov [1] and Moldavsky and coworkers [2]. In these investigations studies were made of the properties of catalysts consisting of oxides of chromium, molybdenum, aluminum, zinc, magnesium, and other metals. It was then established that at 410-440° the dehydrogenation of cyclohexane to benzene could proceed to the extent of 74-77%. In later investigations, however, other workers have shown that the main reaction of dehydrogenation of hydroaromatic hydrocarbons to the corresponding aromatic compounds is accompanied by the formation of intermediate substances and by-products. Plate and Tarasova [3] studied the dehydrogenation of cyclohexane in presence of an aluminum/vanadium oxide catalyst, and in the catalyzates obtained at 500° they found 3.5% of cyclohexene, which they isolated as its insoluble compound with a mercury salt. Herington and Rideal [4] studied the kinetics of dehydrogenation of cyclohexane and its homologs at 450° in presence of an aluminum/chromium oxide catalyst, and they concluded from an analysis of the results that the unsaturated hydrocarbons formed consisted mainly of cycloalkenes, which were intermediate products in the dehydrogenation of hydroaromatic hydrocarbons. There are no indications in the literature of the formation of cyclohexadiene in the dehydrogenation of cyclohexane in presence of oxide catalysts; on the contrary, the absence of this hydrocarbon in the catalyzates has been pointed out [4,5] *.

The catalytic dehydrogenation of ethylbenzene has been investigated by Zelinsky, Balandin, and coworkers [8], Sergienko [9], and Zalkind and Bulavsky [10,11]. This reaction develops at 500-600° in presence of catalysts of approximately the same composition as those used in the dehydrogenation of hydroaromatic hydrocarbons (oxides of Cr, V, Al, Mg, Zn, etc.). Dilution of ethylbenzene with inert gases (CO_2, N_2) considerably increases the yield of styrene.

On the basis of these data from the literature, it might be expected that the main direction of the dehydrogenation of ethylcyclohexane in presence of oxide catalysts at 500-600° would be that leading to the formation of ethylbenzene and styrene. The formation of vinylcyclohexane does not appear very likely. Sergienko [12] showed that passage of vinylcyclohexene over chromic oxide at 400° resulted in its almost complete (99 %) conversion into ethylbenzene. These reaction routes for the dehydrogenation of ethylcyclohexane may be represented by the following scheme.



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* It may be mentioned that the dehydrogenation of hydroaromatic hydrocarbons by Zelinsky's method is carried out at a lower temperature (300°) in presence of metal catalysts (Pt, Pd, Ni): the corresponding aromatic hydrocarbon is then obtained, the formation of by-products or intermediate substances not generally being observed [6,7].

The high temperature catalytic dehydrogenation of ethylcyclohexane has been investigated by Herington and Rideal [4]. The only result of this investigation cited by the authors is the ratio styrene/ethylbenzene in the ethylcyclohexane catalyzate. Unfortunately, the authors do not give many of the fundamental data (space velocities for ethylcyclohexane, styrene and ethylbenzene contents of the catalyzates, method used for the analysis of the catalyzates, etc.), thus lowering the value of this part of the work. In the present investigation the dehydrogenation of ethylcyclohexane has been studied in presence of two catalysts for the passage of ethylcyclohexane or a mixture of its vapor with carbon dioxide at various molar velocities over the catalyst. For comparison, the dehydrogenation of ethylbenzene was studied under analogous conditions.

EXPERIMENTAL

Experimental Procedure

Apparatus and Experimental Method. This is described in a previous paper [13]. Experiments on the dehydrogenation of ethylcyclohexane were alternated with experiments on the dehydrogenation of ethylbenzene. After each experiment the catalyst was regenerated in a current of air so as to preserve constant catalyst activity. In the course of an experiment, 20-25 ml of hydrocarbon was passed. The molar velocity was taken as a fundamental parameter so that it would be possible to compare the results of experiments in which the substances to be dehydrogenated were diluted with carbon dioxide with the results obtained without dilution (changes in molar velocity are inversely proportional to changes in time of contact). The unit adopted for molar velocity was one mole of original substance (or substances) passing per hour over one liter of catalyst, space velocities being expressed in liters of liquid substance passing per hour over one liter of catalyst. The degree of dilution of ethylcyclohexane and ethylbenzene vapors was determined from the ratio of the molar velocity of carbon dioxide to that of the substance being dehydrogenated; it was approximately constant (about 2) in all experiments.

Starting Materials. The ethylbenzene boiled (over sodium) over the range 135.9-136.1° and had n_D^{20} 1.4966 and d_4^{20} 0.8664. The literature [14] gives b.p. 136.1°, n_D^{20} 1.4959 and d_4^{20} 0.8669. Ethylcyclohexane was prepared by the hydrogenation of ethylbenzene in presence of a nickel catalyst under 70-100 atm at 130°. The ethylcyclohexane so prepared was treated twice with concentrated sulfuric acid, washed with water, and dried over $CaCl_2$. On being distilled over sodium through a column of 19 theoretical plates, it came over in the range 130.0-130.2° and had n_D^{20} 1.4340 and d_4^{20} 0.7848. The literature [14] gives b.p. 130.4°, n_D^{20} 1.4332 and d_4^{20} 0.7848. The carbon dioxide was passed through a train of two wash bottles of 10% sodium carbonate solution, a calcium chloride tube, and a rheometer, from which it passed to the reaction tube.

Analysis of Catalyzates. The contents of unsaturated substances in the ethylcyclohexane dehydrogenation catalyzates were determined by Rosenmund's bromometric titration method [15]. Investigation of the ethylcyclohexane catalyzates by the polymerization method (see below) showed that the unsaturated hydrocarbons formed consisted essentially of styrene. In the bromometric calculations, therefore, the molecular weight of styrene was employed.

TABLE 1

Check of the Sulfuric Acid Absorption Method

Expt. No.	Composition of artificial mixture (wt.%)			Amount of mixture taken (g)	Residue of cyclohexane (g)	n_D^{20} of the residue	Ethylcyclohexane content by analysis (wt.%)	Discrepancy (%)
	Styrene	Ethylbenzene	Etnylcyclohexane					
7	14.3	12.6	73.1	7.98	5.7	1.4370	71.3	−1.8
7'	14.3	12.6	73.1	7.99	5.8	1.4376	72.5	−0.6
8	13.5	13.3	73.2	8.17	5.8	1.4340	71.0	−2.2
8'	13.5	13.3	73.2	7.94	5.5	1.4338	69.4	−3.8
6	23.2	21.3	55.5	8.22	4.3	1.4340	52.3	−3.2
6'	23.2	21.3	55.5	8.19	4.7	1.4483	57.5	+2.0
9	20.9	25.4	53.7	8.15	4.3	1.4438	52.8	−0.9
9'	20,9	25.4	53.7	8.19	4.6	1.4475	56.2	+2.5

The contents of unchanged ethylcyclohexane in the catalyzates were determined from the amount of the residue after absorption of unsaturated hydrocarbons and ethylbenzene with concentrated sulfuric acid (monohydrate). In order to avoid heating and polymerization of styrene when performing this operation, a cylinder containing a quantity of monohydrate (10 ml) and a weighed amount of catalyzate (volume 10 ml) was cooled to −10-15°. The cylinder was then shaken carefully and again cooled, after which shaking was continued in a mechanical shaker. After separation of the sulfuric acid layer, the operation was repeated, the only difference being that the quantity of monohydrate taken was 5 ml. This method was checked on mixtures of styrene, ethylbenzene, and ethylcyclohexane. The results of these checks are given in Table 1.

The weight of residue was determined from its volume and the specific gravity of ethylcyclohexane. The refractive indices of the residues were somewhat greater than the value for ethylcyclohexane, probably owing to the presence of sulfonation of polymerization products. The difference between true and found content of ethylcyclohexane in the mixture did not exceed 3.8%.

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Chromium/Molybdenum Oxide Catalyst

The dehydrogenation of ethylcyclohexane in presence of an aluminum/chromium/molybdenum oxide catalyst was carried out at 495° in presence of carbon dioxide as diluent. The results of this series of experiments are given in Table 2 and Fig. 1.

A four-fold increase in the total molar velocity of ethylcyclohexane and carbon dioxide (from 1.7 to 7.1) led to a reduction in the ethylbenzene content of the ethylcyclohexane catalyzate from 55.5% to 26.5%, but had no effect on the content of unsaturated hydrocarbons (5-6%).

TABLE 2

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Chromium/Molybdenum Oxide Catalyst at 495° in Presence of Carbon Dioxide as Diluent

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/liter-hr)	Molar velocity (mole/liter-hour)			Degree of dilution	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt.%)	
			Hydrocarbon	CO_2	Total			Unsaturated hydrocarbon (styrene)	Ethylbenzene
56	Ethylcyclohexane	0.08	0.6	1.1	1.7	1.8	70	5.0	55.5
60	"	0.14	1.0	2.0	3.0	2.0	63	6.0	42.5
62	"	0.22	1.6	3.2	4.8	2.0	63	4.9	29.1
52	"	0.30	2.1	5.0	7.1	2.4	81	5.2	26.5
57	Ethylbenzene	0.09	0.8	1.1	1.9	1.4	74	19.2	–
59	"	0.12	1.0	2.0	3.0	2.0	83	23.3	–
58	"	0.19	1.5	3.4	4.9	2.3	84	22.2	–
53	"	0.30	2.5	5.0	7.5	2.0	86	19.9	–

Change, over approximately the same range, in the molar velocities of ethylbenzene and CO_2 was also practically without effect on the styrene content of the catalyzate (19.2-23.3%).

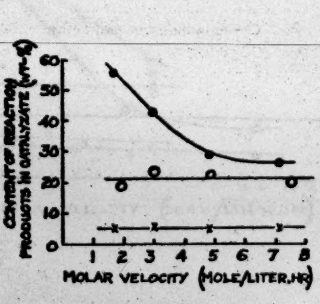

Fig. 1. Dehydrogenation of ethylcyclohexane and ethylbenzene in presence of an aluminum/chromium/molybdenum oxide catalyst at 495° in presence of carbon dioxide as diluent:
× – unsaturated substances from ethylcyclohexane;
● – ethylbenzene from ethylcyclohexane;
○ – styrene from ethylbenzene.

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Vanadium Oxide Catalyst

All experiments in presence of an aluminum/vanadium oxide catalyst were carried out at 547°. The dehydrogenation of ethylcyclohexane and ethylbenzene was performed both in presence of carbon dioxide as diluent for the vapor of the reactant, and also in absence of diluent.

The results of experiments on the dehydrogenation of ethylcyclohexane and ethylbenzene over an aluminum/vanadium oxide catalyst in presence of carbon dioxide as diluent are given in Table 3 and Fig. 2. Rise in temperature led to increase in the concentrations of reaction products in the catalyzates. Change in the total molar velocities of ethylcyclohexane and CO_2 over the same range (1.7 to 7.2) as before led to a reduction of the ethylbenzene content of the ethylcyclohexane catalyzates from 67.5% to 38.9%, but was accompanied by the formation of practically unchanged amounts of unsaturated hydrocarbons (10.4-13.9%).

The styrene content of the catalyzates from the dehydrogenation of ethylbenzene in presence of CO_2 also remained practically constant (28.6-31.1%) as the total molar velocity changed from 1.6 to 7.3; the somewhat higher degree of dehydrogenation in Expt. 104 resulted probably from an increase in the degree of dilution to 2.4.

TABLE 3

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Vanadium Oxide Catalyst at 547° in Presence of Carbon Dioxide as Diluent

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/liter-hr)	Molar velocity (mole/liter-hour)			Degree of dilution	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt %)	
			Hydrocarbon	CO_2	Total			Unsaturated hydrocarbon (styrene)	Ethylbenzene
72	Ethylcyclohexane	0.08	0.6	1.1	1.7	1.8	80	12.3	67.5
75	"	0.13	0.9	2.0	2.9	2.1	77	13.9	62.5
78	"	0.22	1.5	3.0	4.5	2.0	85	11.6	52.8
71	"	0.31	2.2	5.0	7.2	2.3	86	10.4	38.9
76	Ethylbenzene	0.06	0.5	1.1	1.6	2.2	74	28.6	–
74	"	0.12	1.0	2.0	3.0	2.0	83	29.5	–
79	"	0.29	2.4	5.0	7.4	2.1	89	31.1	–
70	"	0.30	2.4	5.0	7.4	2.1	89	29.9	–
104	"	0.26	2.2	5.1	7.3	2.4	81	35.3	–

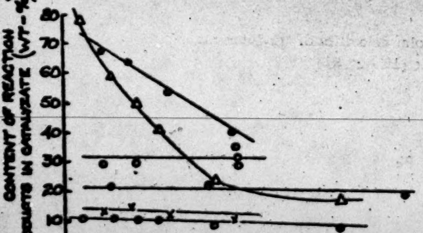

Fig. 2. Dehydrogenation of ethylcyclohexane and ethylbenzene in presence of an aluminum/vanadium oxide catalyst at 547°:

X – unsaturated substances from ethylcyclohexane (CO_2 diluent);

● – ethylbenzene from ethylcyclohexane (CO_2 diluent);

○ – styrene from ethylbenzene (CO_2 diluent);

⊙ – unsaturated substances from ethylcyclohexane (no diluent);

△ – ethylbenzene from ethylcyclohexane (no diluent);

◐ – styrene from ethylbenzene (no diluent).

The dehydrogenation of ethylcyclohexane and ethylbenzene in absence of diluent was carried out with the same portion of aluminum/vanadium oxide catalyst. The results of these experiments are given in Table 4. An approximately seventeenfold increase in the molar velocity of ethylcyclohexane (from 0.7 to 11.7) resulted in a reduction in the ethylbenzene content of the catalyzates from 78.6% to 17.4%, whereas the concentration of unsaturated substances diminished only from 10.4% to 7.3%. There was a similar small change in the styrene content of the ethylbenzene dehydrogenation catalyzate (from 20.7% to 18.8%) for a change in molar velocity from 2.0 to 14.5.

TABLE 4

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Vanadium Oxide Catalyst at 547°, No Diluent Being Present

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/liter-hr)	Molar velocity (mole/liter-hr)	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt.%)	
					Unsaturated hydrocarbon	Ethylbenzene
99	Ethylcyclohexane	0.11	0.7	67	10.4	78.6
98	"	0.29	2.0	77	11.1	58.9
100	"	0.45	3.1	85	9.9	49.6
101	"	0.56	4.0	83	9.9	40.6
133	"	0.90	6.3	93	8.0	23.6
134	"	1.67	11.7	92	7.3	17.4
103	Ethylbenzene	0.24	2.0	87	20.7	–
97	"	0.76	6.2	93	23.0	–
102	"	1.75	14.5	94	18.8	–

A comparison of the results of these series of experiments (with and without a carbon dioxide diluent; see Fig. 2) shows that an equal dilution of ethylcyclohexane vapor and ethylbenzene vapor leads to the same relative increase in the concentration of unsaturated hydrocarbons (styrene). At the dilution investigated (about 2), the concentrations of unsaturated substances in the ethylcyclohexane catalyzates and of styrene in the ethylbenzene catalyzates increased by about 30%: the styrene concentration in the ethylbenzene catalyzates was 18.8-23.0% in absence of diluent and 28.6-31.1% in presence of diluent; the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates was 7.3-11.1% without diluent and 10.4-13.9% qith diluent. The reduction in the degree of dehydrogenation of ethylcyclohexane to ethylbenzene in experiments without diluent, as compared with the experiments in which a carbon dioxide diluent was used, is to be explained, evidently, by a certain loss in catalyst activity with respect to the dehydrogenation of the cyclohexane ring. The activity of the catalyst for the dehydrogenation of ethylbenzene to styrene remained practically constant, as will be seen by a comparison of the results of Expts. 70 and 104 (Table 3), which were performed at the beginning and end, respectively, of the trials with the given portion of catalyst.

Determination of Styrene in Ethylcyclohexane Catalyzates by the Polymerization Method

It was pointed out above that the content of unsaturated hydrocarbons in ethylcyclohexane catalyzates was determined by bromometric titration. The high concentrations of ethylbenzene in these catalyzates gave reason to suppose that the unsaturated hydrocarbons formed consisted essentially of styrene. It was necessary to determine, however, whether any other unsaturated hydrocarbons were formed. For this purpose the ethylcyclohexane catalyzates were investigated by the polymerization method. Marukyan [16] has examined the applicability of the bromometric titration and polymerization methods for the determination of styrene and has found good agreement (within 1%) between the results obtained by these methods. In one of our previous investigations [17] we obtained similar results. On the other hand, there is nothing in the literature concerning the tendency of cyclohexene or ethylcyclohexene to polymerize. The tendency of vinylcyclohexane to polymerize (under prolonged treatment at 170°) was investigated by Shorygin and Shorygina [18]: the authors concluded that this hydrocarbon is not able to polymerize and shows only an "incipient" tendency to form dimers. The polymerization method, therefore, has enabled more accurate results to be obtained for the styrene contents of the catalyzates than could be obtained by bromometric titration.

The ethylcyclohexane catalyzates obtained in the experiments with an aluminum/vanadium oxide catalyst at 547° in absence of diluent (see Table 4) were united. The united catalyzate contained 9.0% of unsaturated hydrocarbons (calculated as styrene) as determined by bromometric titration. A 31.2 g sample of the united catalyst, with an addition of 0.4 g of benzoyl peroxide, was sealed in a tube and maintained at 150-160° for 80 hours, after which it was fractionated at 50 mm pressure. The fractionation yielded 2.3 g of solid polymer (instead of the calculated 2.8 g) and 28.3 g nonpolymerized catalyzate. The amount of polymer obtained was 6.1% of weight of catalyzate taken (after making a correction for the added benzoyl peroxide). It follows from these results that the united catalyzate contained 6.1% of styrene and 2.9% of other, nonpolymerizing unsaturated hydrocarbons. The content of the latter was determined also by another method. The nonpolymerizing part of the catalyzate, which was distilled from the polymer at 50-60° and 50 mm pressure, had n_D^{20} 1.4560 and contained 38% of ethylbenzene and 4.5% of unsaturated hydrocarbons. This content of nonpolymerizing unsaturated hydrocarbons in the distillate corresponds to 4.1% of them in the united catalyzate.

The liquid distilled from the polymer was treated with monohydrate in order to remove aromatic and unsaturated hydrocarbons. The residue obtained contained no unsaturated substances, distilled over Na at 130-131°, and had d_4^{20} 0.7867 and n_D^{20} 1.4321. These constants are close to those of ethylcyclohexane (b.p. 130.4°, d_4^{20} 0.7840 and n_D^{20} 1.4332) [14], and they indicate that very little destructive decomposition of ethylcyclohexane occurs in the course of its dehydrogenation. The nonpolymerizing unsaturated hydrocarbons were therefore formed by the dehydrogenation of ethylcyclohexane, and probably consisted of ethylcyclohexene.

The united ethylcyclohexane catalyzate, therefore, contained 6.1% of styrene and 3-4% of unsaturated hydrocarbons of different character. The unsaturated part of the united catalyzate consisted, therefore, of about 65% of styrene and about 35% of nonpolymerizing unsaturated hydrocarbons. It follows from a comparison of these results with those described previously that the main direction of the dehydrogenation of ethylcyclohexane is that leading to the formation of ethylbenzene and styrene, the reaction being accompanied, however, by the formation of small amounts of unsaturated hydrocarbons of another character.

DISCUSSION OF RESULTS

The main products of the high temperature catalytic dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. The ethylbenzene content of the ethylcyclohexane catalyzates rapidly falls as the molar velocity rises, but the concentration of unsaturated hydrocarbons (which consist mainly of styrene) remains practically constant. The styrene content of the catalyzates from the dehydrogenation of ethylbenzene also remains practically unchanged as the molar velocity varies over a wide range, and it is several times as great as the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates.

The results obtained permit us to conclude that the dehydrogenation of ethylcyclohexane proceeds in two stages:

$$\text{ethylcyclohexane} \longrightarrow \text{ethylbenzene} \longrightarrow \text{styrene}.$$

The question arises, however, of the causes of the nondependence of styrene formation from ethylcyclohexane on the degree of aromatization of ethylcyclohexane. It is interesting to note that other investigators have observed a constant concentration of cyclohexene in catalyzates from cyclohexane having different degrees of aromatization. Plate and Druzhchits [5], for example, studied the reactions of cyclohexane and cyclohexane-cyclohexene mixtures (10, 20 and 30% of cyclohexene) in presence of a chromic oxide catalyst at 420-500°. They concluded that "irrespective of the composition of the original mixture, the olefin content of the catalyzate evidently tends to a definite limiting value, possibly to an equilibrium value; under the conditions studied the limit was at 6-8% of olefins in the mixture." Herington and Rideal [4] investigated the dehydrogenation of cyclohexane and mixtures of cyclohexane with cyclohexene (1, 2 and 3%) at 450°, and they also concluded that a stationary concentration of unsaturated hydrocarbons was established (1.65-1.73% in the catalyzate); the authors explained the constant concentration of unsaturated hydrocarbons in the catalyzates by kinetic factors; namely, by the ratio of the rates of dehydrogenation of cyclohexane to cyclohexene and of cyclohexene to benzene. Thermodynamic equilibrium cannot occur here: according to our calculations (based on the data of Korobov and Frost [19]), the equilibrium cyclohexane $\rightleftharpoons$ cyclohexene + H_2 at 427-527° is displaced to the right by 89.6-98.7%.

On the other hand, it might be expected that the approximately constant concentration of unsaturated hydrocarbons in ethylcyclohexane dehydrogenation catalyzates could be the result of the existence of thermodynamic equilibrium in the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane:

$$\text{ethylcyclohexane} \longrightarrow \text{ethylbenzene} + 3H_2 \rightleftharpoons \text{styrene} + 4H_2$$

We have previously shown [13] that the constant styrene contents of ethylbenzene dehydrogenation catalyzates over a wide range of molar velocities result from the fact that this reaction attains a state of thermodynamic equilibrium. The identical relative increase in content of unsaturated products in catalyzates for identical dilution of ethylbenzene and ethylcyclohexane with carbon dioxide (see above) evidently results from the same cause: the inert diluent displaces the equilibrium in the direction of styrene. With the object of verifying the correctness of this hypothesis, the relevant thermodynamic calculation has been made.

SUMMARY

1. An investigation has been made of the high temperature dehydrogenation of ethylcyclohexane and ethylbenzene in presence of two catalysts at different temperatures (495° and 547°) and with and without a carbon dioxide diluent.

2. It has been found that the main products of the dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. At the same time small amounts of unsaturated "by-products" are formed (probably ethylcyclohexene).

3. It has been shown that the ethylbenzene content of ethylcyclohexane catalyzates falls sharply as the molar velocity is increased, but the concentration of unsaturated products (mainly styrene) remains practically constant and is independent of the degree of aromatization of the ethylcyclohexane. The styrene content of the ethylbenzene dehydrogenation catalyzates also remains practically constant when the molar velocity is varied over a wide range, and it is several times as great as the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates.

4. It has been established, on the basis of these results, that the catalytic dehydrogenation of ethylcyclohexane proceeds in two stages: ethylcyclohexane → ethylbenzene → styrene.

5. It has been shown that identical dilution of ethylcyclohexane and ethylbenzene with carbon dioxide (a dilution of 2) leads to identical relative increase (by one third) in the content of unsaturated hydrocarbons in the catalyzates.

6. It has been suggested that the nondependence of the styrene content of ethylcyclohexane catalyzates on the degree of aromatization of the ethylcyclohexane results from the fact that the dehydrogenation of ethylbenzene, formed from ethylcyclohexane, attains a state of thermodynamic equilibrium.

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HIGH TEMPERATURE CATALYTIC DEHYDROGENATION OF ETHYLCYCLOHEXANE

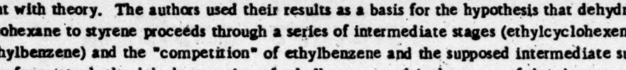
COMMUNICATION 2. THERMODYNAMIC EQUILIBRIUM IN THE DEHYDROGENATION OF ETHYLBENZENE UNDER THE CONDITIONS OF ITS FORMATION FROM ETHYLCYCLOHEXANE

I. I. Levitsky and N. I. Shuikin

The thermodynamic equilibrium ethylbenzene ⇌ styrene + H_2, occurring under the conditions of formation of these substances from ethylcyclohexane, has been investigated by Herington and Rideal [1] at 500° in presence of an aluminum/chromium oxide catalyst. These authors found that the experimentally determined ratio styrene/ethylbenzene was twice as small as the value calculated from the constant K_E for the dehydrogenation of ethylbenzene. From these results the authors concluded that the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane does not attain a state of equilibrium, although, as was shown in the same investigation, the results for the dehydrogenation of pure ethylbenzene under the same conditions are in good agreement with theory. The authors used their results as a basis for the hypothesis that dehydrogenation of ethylcyclohexane to styrene proceeds through a series of intermediate stages (ethylcyclohexene, ethylcyclohexadiene, ethylbenzene) and the "competition" of ethylbenzene and the supposed intermediate substances for the catalyst surface retards the dehydrogenation of ethylbenzene and is the cause of the absence of equilibrium under these conditions.

We must point out, however, that the discrepancy, referred to above, between theoretical and experimental styrene/ethylbenzene ratios corresponds to an extremely small difference in the theoretical and experimental values of the yield of styrene from ethylcyclohexane: it is, for example, easy to calculate that for 60% aromatization of ethylcyclohexane at 500° (according to Herington and Rideal K_E = 0.0304) the difference is only 1.3%. The authors do not indicate what method they used for the determination of styrene in presence of other unsaturated hydrocarbons, although the probable error in the usual methods for the analysis of unsaturated hydrocarbons differs little from the difference stated above; consequently, inferences, based on such figures, concerning the absence of equilibrium and the mechanism of the reaction can scarcely be convincing.

In our previous communication [2] it was pointed out that the ethylbenzene content of catalyzates from the dehydrogenation of ethylcyclohexane falls sharply as the molar velocity increases, whereas the corresponding styrene content remains approximately constant, practically independent of the degree of aromatization of ethylcyclohexane. It was also found [3] that the dehydrogenation of pure ethylbenzene attains a state of thermodynamic equilibrium over a wide range of molar velocities. These results gave reason to suppose that, in the dehydrogenation of the ethylbenzene formed from ethylcyclohexane, a state of thermodynamic equilibrium was practically attained:



The first stage of this reaction is determined by kinetic factors: the equilibrium ethylcyclohexane ⇌ ethylbenzene + $3H_2$ is displaced to the extent of 100% to the right even at 400° [4]. It is therefore clear that absolute equilibrium of the second stage is impossible owing to the continuous formation of ethylbenzene; for absolute equilibrium to be attained complete independence of the dehydrogenation of ethylbenzene of the time of contact would be necessary. In the present paper a thermodynamic calculation is made for the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane, and a comparison is made between the theoretical and experimental results.

The calculation of equilibrium yields of styrene in the dehydrogenation of ethylcyclohexane is complicated by three supplementary factors*: a) the concentration of ethylbenzene is not constant, but changes with the degree of dehydrogenation of the ethylcyclohexane ring; b) the hydrogen formed by the dehydrogenation of the ethylcyclohexane ring displaces the equilibrium to the left; c) the original ethylcyclohexane, as a diluent for the components of the equilibrium mixture, displaces the equilibrium to the right.

These three factors, in their turn, depend on the degree of dehydrogenation of the ethylcyclohexane ring and so on the time of contact, activity of the catalyst, etc. These factors must be taken into account in a thermodynamic calculation of the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane:

$$\underset{4}{C_6H_{11}C_2H_5} = \underset{1}{C_6H_5C_2H_5} + \underset{3}{3H_2} = \underset{2}{C_6H_5CH{=}CH_2} + \underset{3}{4H_2}$$

When one mole of ethylcyclohexane is dehydrogenated with formation of x moles of ethylbenzene and the ethylbenzene formed is then dehydrogenated (to a state of equilibrium) with formation of y moles of styrene, the equilibrium mixture consists of:

Ethylbenzene	$n_1 = x - y$	moles
Styrene	$n_2 = y$	"
Hydrogen	$n_3 = 3x + y$	"
Ethylcyclohexane (inert diluent)	$n_4 = n_{in} = 1 - x$	"

By insertion of these expressions in the equation for the equilibrium constant for the dehydrogenation of ethylbenzene [3], we obtain:

$$K_E = \frac{n_2 n_3}{n_1(n_1 + n_2 + n_3 + n_{in})} = \frac{y(3x + y)}{(x - y)(1 + 3x + y)} \tag{1}$$

and after rearrangement:

$$(1 + K_E)y^2 + (3x + 2K_E x + K_E)y - (K_E x + 3K_E x^2) = 0 \tag{2}$$

The value of x in equation (2) corresponds to the sum of the yields of ethylbenzene and styrene from ethylcyclohexane ("degree of aromatization" of ethylcyclohexane). Knowing the value of the equilibrium constant K_E we may calculate the equilibrium yields of styrene y from ethylcyclohexane for various degrees of aromatization x of the latter.** This calculation has been performed for the temperature 547°. The equilibrium constant K_E calculated by the graphical method from the data in [5], which are computed from spectrum measurements, was found to be 0.0737 at 547°. The results of calculations of y from equation (2) ($K_E = 0.0737$) are presented in Table 1 and in the figure (upper curve). Complete dehydrogenation of ethylcyclohexane to ethylbenzene (or dehydrogenation of one mole of ethylbenzene in admixture with three moles of hydrogen) leads to an equilibrium yield of styrene of 8.9%. We may point out that the equilibrium degree of dehydrogenation of pure ethylbenzene to styrene for $K_E = 0.0737$ is 26.2%. Changes in the degree of aromatization of ethylcyclohexane are accompanied by extremely insignificant changes in the equilibrium yields of styrene: when the degree of aromatization of ethylcyclohexane is reduced by 20%, the

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*Supplementary to the usual factors: the value of K . the dilution, etc.

**The calculation of the theoretical yields of styrene from ethylcyclohexane may be performed also by another method, without taking the intermediate formation of ethylbenzene into account. When x moles of ethylbenzene and y moles of styrene are formed (by one or another route) from one mole of ethylcyclohexane, the mixture consists of: $n_1 = x$, $n_2 = y$, $n_3 = 3x + 4y$ and $n_{in} = 1 - (x + y)$. After insertion of these expressions in equation (1), we obtain:

$$4y^2 + (3x - 4K_E x)y - (K_E x + 3K_E x^2) = 0. \tag{3}$$

In equation (3) the value of x corresponds to the yield of ethylbenzene from ethylcyclohexane. Calculations of theoretical yields of styrene from equations (2) and (3) yield identical results.

equilibrium yield of styrene falls by only 1.4%. These results can supply the explanation of the approximate constancy, noted above, in the styrene content of ethylcyclohexane dehydrogenation catalyzates over a wide range of degree of aromatization.

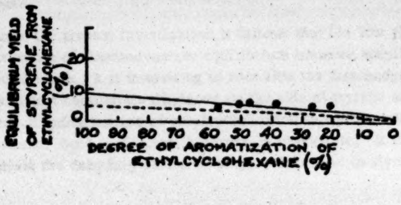
A comparison of the calculated and experimental yields of styrene from ethylcyclohexane was made on the basis of the results given in Table 4 of our previous communication [2]. These results refer to a series of experiments in which ethylcyclohexane and ethylbenzene were dehydrogenated in absence of diluent at 547° in presence of an aluminum/vanadium oxide catalyst.

It was shown in the same paper that the unsaturated hydrocarbons in the united catalyzate from this series contained 65% of styrene. From this value, the yields of catalyzates, and results of the bromometric determination of unsaturated hydrocarbons, the yields of styrene, based on the ethylcyclohexane passed, were calculated for the separate experiments. Also, on the basis of the degree of aromatization of ethylcyclohexane and the value of K_E = 0.0737 the theoretical yields of styrene from ethylcyclohexane were calculated. The results of these calculations are given in Table 2. A comparison of the theoretical and experimental yields of styrene is shown in the graph: The difference in theoretical and experimental yields (see column 11, Table 2) does not exceed 1.3%, which is

TABLE 1

Equilibrium Yields of Styrene from Ethylcyclohexane at 547° for Different Degrees of Aromatization of the Latter (K_E = 0.0737)

Degree of aromatization of ethylcyclohexane (%)	Equilibrium yields of styrene from ethylcyclohexane (%)
100	8.9
80	7.5
60	6.1
40	4.7
20	3.2



Equilibrium yields of styrene from ethylcyclohexane at 547° for various degrees of aromatization of the latter. The upper curve is calculated for K_E = 0.0737, computed from spectrum data. The lower curve is calculated for K_E = 0.0374, computed from experimental data. ● – experiments on the dehydrogenation of ethylcyclohexane over V_2O_5-Al_2O_3.

TABLE 2

Dehydrogenation of Ethylcyclohexane without Diluent at 547° in Presence of an Aluminum/Vanadium Oxide Catalyst

Expt. No.	Molar rate of passage of ethylcyclohexane (mole/liter-hr)	Yield, on ethylcyclohexane passed, of catalyzate (%)	Content of reaction products in catalyzate (%)		Yield, on ethylcyclohexane passed, of reaction products (%)		Degree of aromatization of ethylcyclohexane (%) *	Yield, on ethylcyclohexane passed, of styrene (%)	Theoretical yield of styrene from ethylcyclohexane (%)	Discrepancy (%)
			Ethylbenzene	Unsaturated hydrocarbon	Ethylbenzene	Unsaturated hydrocarbon				
1	2	3	4	5	6	7	8	9	10	11
99	0.7	67	78.6	10.4	52.7	7.0	57.3	4.6	5.9	−1.3
98	2.0	77	58.9	11.1	45.4	8.5	50.9	5.5	5.5	0
100	3.1	85	49.6	9.9	42.2	8.4	47.7	5.5	5.2	+0.3
101	4.0	83	40.6	9.9	33.7	8.2	39.0	5.3	4.6	+0.7
133	6.3	93	23.6	8.0	21.9	7.4	26.7	4.8	3.7	+1.1
134	11.7	92	17.4	7.3	16.0	6.7	20.4	4.4	3.2	+1.2

*The degree of aromatization of ethylcyclohexane was obtained by adding the values in columns 6 and 9.

close to the probable error of the analytical method used. These results show that the reaction under consideration has practically attained a state of thermodynamic equilibrium.

In our investigation [3] of the part played by inert diluents in the catalytic dehydrogenation of ethylbenzene, it was shown that the results of experiments on the dilution of ethylbenzene with nitrogen and toluene were in good agreement with calculations from the experimental equilibrium constant. It was of interest to calculate the yields of styrene from ethylcyclohexane on the basis of a value of K_g calculated from experimental quantities. In Table 4 of the previous communication [2] results were given of ethylbenzene dehydrogenation experiments that alternated with the ethylcyclohexane dehydrogenation experiments considered above. In these experiments the average yield of styrene was 19.0% on the ethylbenzene passed, and the corresponding value of K_g is 0.0374. The results of calculations, on the basis of $K_g = 0.0374$, of the yields of styrene from ethylcyclohexane are given by the lower graph in the figure. The yields of styrene calculated in this way are 2.5-2.8% less (except Expt. 99) than the experimental values obtained in the dehydrogenation of ethylcyclohexane. It should be remembered that discrepancies of a similar nature were observed by us [3] also in the dehydrogenation of ethylbenzene in admixture with hydrogen: the experimental yields of styrene were 3-4% greater than those calculated from the experimental K_g It is probable that these discrepancies have the same cause. The low concentrations of styrene in the catalyzates both of ethylcyclohexane and of ethylbenzene when diluted with hydrogen caused a lower degree of polymerization than that occurring in experiments with pure ethylbenzene, on the results of which the calculation of the experimental K_g is based.

From the present investigation it follows that the low yields of styrene from ethylcyclohexane are the result of the presence of thermodynamic equilibrium between ethylbenzene, styrene, and hydrogen, as formed from ethylcyclohexane. It is interesting to note that the thermodydnamic equilibrium ethylcyclohexane $\rightleftharpoons$ styrene $+ 4H_2$ is almost completely displaced on the side of styrene at 500-600°. The effecting of this reaction demands the direct dehydrogenation of ethylcyclohexane to styrene without the intermediate or subsequent formation of ethylbenzene. Such a reaction, however, is impossible: it is scarcely possible for there to be a catalyst that will initiate the dehydrogenation of ethylcyclohexane to styrene, but cannot hydrogenate styrene to ethylbenzene.

SUMMARY

1. A thermodynamic calculation has been performed for the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane at 547°. Equilibrium yields of styrene from ethylcyclohexane change by only 1.4% when the degree of aromatization of ethylcyclohexane changes by 20%.

2. It has been shown that the experimental yields of styrene from ethylcyclohexane coincide (within the limits of the accuracy of the analysis) with theoretical figures. Hence, the dehydrogenation of ethylbenzene formed from ethylcyclohexane attains equilibrium.

3. It has been established that the nondependence of the yields of the final product of the dehydrogenation of ethylcyclohexane (styrene) on changes over a wide range in the progress of the intermediate stage of this reaction (yield of ethylbenzene) results from the fact that the dehydrogenation of ethylbenzene formed from ethylcyclohexane attains an equilibrium.

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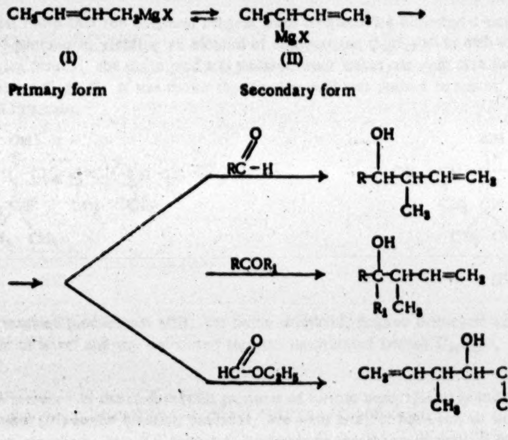
REACTION OF THE GRIGNARD REAGENT FROM 3-CHLORO-2,4-DIMETHYL-1-PENTENE WITH 2,4-DIMETHYL-3-PENTANONE, ETHYL FORMATE, AND AMYL BUTYRATE

V. A. Ponomarenko and T. Ya. Tolkacheva

The investigations of Young and Roberts with coworkers [1-5] and Ou Kiun Houo [6] have revealed an extremely interesting example of the allyl rearrangement; namely, the tendency for the reaction of 2-butenylmagnesium halide with a number of carbonyl compounds* to yield alcohols corresponding to the secondary form of the Grignard reagent (II):



$$CH_3-CH=CH-CH_2MgX \rightleftarrows \underset{MgX}{CH_3-CH}-CH=CH_2 \longrightarrow$$

where X = Br, Cl.

It should be noted that it is immaterial as regards the result of the process whether we take pure isomeric halobutenes for the reaction ($CH_3-CH=CH-CH_2X$ or $CH_3-\underset{X}{C}H-CH=CH_2$), or the mixture of these that is readily formed as a result of the allyl rearrangement $CH_3-CH=CH-CH_2X \rightleftarrows CH_3-\underset{X}{C}H-CH=CH_2$. Among the carbonyl compounds that have been studied in connection with this reaction are the following: formaldehyde [2,10], acetaldehyde [2,6,7], propionaldehyde [6,7], acrolein [6,7], benzaldehyde [7], acetone [2], 2,4-dimethyl-3-pentanone [3], 2,2,4-trimethyl-3-pentanone [4], 2,2,4,4 -tetramethyl-3-pentanone [4], 2',4',6'-trimethylacetophenone [5], 2',4',6'-trimethylisobutyrophenone [4], benzophenone [4], and ethyl formate [9]. In reactions with ketones, steric hindrance effects are found; in the case of 2,4-dimethyl-3-pentanone [3], it is manifested by the simultaneous formation of the isomeric alcohol

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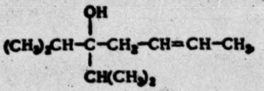
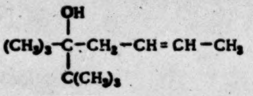
*A similar tendency is shown in the reactions of 2-butenylmagnesium halide with CO_2 [1,2], ethyl orthoformate [9,10], and phenyl isocyanate [9].



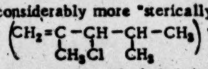
$$(CH_3)_2CH-\underset{\displaystyle CH(CH_3)_2}{\overset{\displaystyle OH}{C}}-CH_2-CH=CH-CH_3$$

corresponding to the primary form of the Grignard reagent (I) (15% for 2-butenylmagnesium bromide and 6% for 2-butenylmagnesium chloride).*

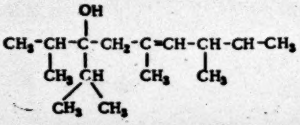
2,2,4,4-Tetramethyl-3-pentanone; i.e., a ketone in which pronounced steric hindrance occurs, forms only the alcohol corresponding to the primary form of the reagent, 2-butenylmagnesium halide (I):



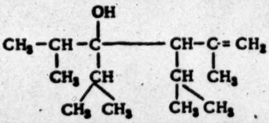
$$(CH_3)_3-\underset{\displaystyle C(CH_3)_3}{\overset{\displaystyle OH}{C}}-CH_2-CH=CH-CH_3$$

We considered it to be of interest to study the reaction of considerably more "sterically hindered" unsaturated Grignard reagents prepared from 3-chloro-2,4-dimethyl-1-pentene  $\left(CH_2=\underset{\displaystyle CH_3}{C}-\underset{\displaystyle Cl}{CH}-\underset{\displaystyle CH_3}{CH}-CH_3\right)$ with 2,4-dimethyl-3-pentanone and determine: 1) the possibility, in general, of forming a tertiary alcohol, it being known that saturated, less "sterically hindered," secondary alkylmagnesium halides** do not form the corresponding tertiary alcohols, but merely reduce the 2,4-dimethyl-3-pentanone to 2,4-dimethyl-3-pentanol, and 2) the effect on the course of the reaction of greater steric hindrance in our alkenylmagnesium halide (than in 2-butenylmagnesium halide), if a tertiary alcohol is formed.

It was found that the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene reacts fairly readily with 2,4-dimethyl-3-pentanone, yielding an alcohol of composition $C_{14}H_{27}OH$ in 40% yield. Ozonization of this alcohol gave the following results: the main products isolated were isobutyric acid (via the amide) and an unsaturated ketone of composition $C_{10}H_{18}O$; it was shown that formic acid was present in traces. Hence, of the two alcohols that are possible in this case:



(III)

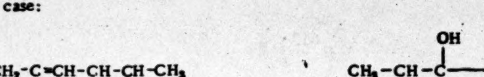


(IV)

the main reaction product was (III). On being ozonized, it gave isobutyric acid and a hydroxy ketone, which lost a molecule of water and was converted into the unsaturated ketone $C_{10}H_{18}O$. This ketone gave a semicarbazone of m.p. 195°.

The presence in the ozonization products of formic acid evidently indicates the presence of a small amount of the alcohol (IV) in the reaction products. We were unable, however, to isolate the corresponding ketone. In its reaction, therefore, with 2,4-dimethyl-3-pentanone the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentane behaves in an essentially different manner from 2-butenylmagnesium chloride, the explanation evidently lying in the greater steric hindrance that is present.

In 1947 Tuot and Guyard [8], who were trying to prepare certain branched hydrocarbons having 15 and 16 carbon atoms, were unable to obtain the alcohols required as starting materials by the reactions:

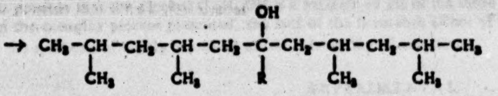


$$CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2Br+Mg+R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OC_2H_5}\longrightarrow$$

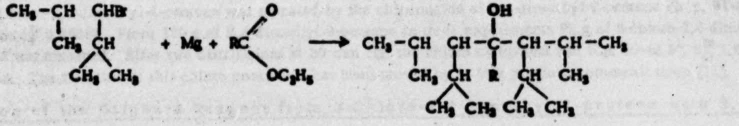
---

* The remaining 85% and 94% respectively is to be assigned to alcohol formed from the secondary form of the Grignard reagent (II). The total yield of alcohols is 84-89%.

** These include isopropylmagnesium bromide and sec-butylmagnesium bromide.



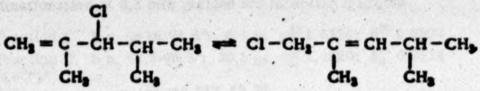
$$\rightarrow CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\overset{OH}{\underset{R}{C}}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_3 \qquad (1)$$



(2)

where R = CH_3, H. Tuot and Guyard explained their lack of success by the presence in the alkyl halides of steric hindrance, which resulted in side reactions: formation of 2,4-dimethylpentane, 2,4-dimethyl-1-pentene, 2,4-dimethyl-2-pentene, 3,5-dimethyl-1-hexanol, and 2-isopropyl-3-methyl-1-butanol.

We did not undertake the task of studying the structure of the alcohols obtained by reaction of the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene with ethyl formate and with amyl butyrate; we attempted only to establish the nature of the effect on the course of the synthesis of the double bond in the β-position in the allyl rearrangement system from 3-chloro-2,4-dimethyl-1-pentene:

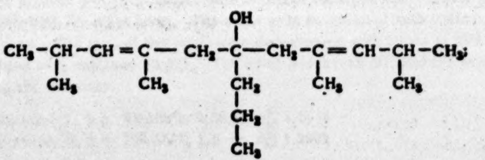


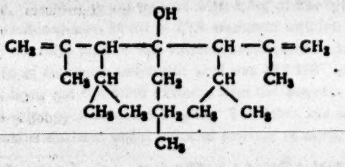
$$CH_2=\underset{CH_3}{C}-\overset{Cl}{CH}-\underset{CH_3}{CH}-CH_3 \rightleftharpoons Cl-CH_2-\underset{CH_3}{C}=CH-\underset{CH_3}{CH}-CH_3,$$

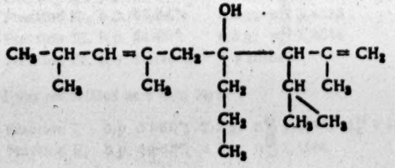
the structural analog of Tuot and Guyard's bromides.

Reaction with ethyl formate yielded the formic ester of an alcohol $C_{15}H_{27}OH$ in 23% yield; it was readily hydrolyzed, yielding the alcohol $C_{15}H_{27}OH$. With amyl butyrate the yield of alcohol attained 36%.

It is of interest that in this case no ester was formed. Ozonization of this alcohol gave formic and isobutyric acids. As we did not analyze the neutral products, we were unable to assign the alcohol any particular one of the three possible structures:







It is possible that the alcohol $C_{18}H_{33}OH$ is a mixture of all of the three forms, with one of them predominating. In spite of the complex picture presented, the fact of the favorable effect of a double bond β to the halogen on the course of the synthesis of highly branched alcohols is worthy of attention.

EXPERIMENTAL

3-Chloro-2,4-dimethyl-1-pentene

3-Chloro-2,4-dimethyl-1-pentene was prepared by the chlorination of 2,4-dimethyl-2-pentene (b.p. 81-82.5°; n_D^{20} 1.4035; d_4^{20} 0.6948). From 189 g of 2,4-dimethyl-2-pentene in three experiments 98 g of 3-chloro-2,4-dimethyl-1-pentene was obtained. After two distillations at 30 mm Hg, the chloro compound had b.p. 40-42.5°, n_D^{20} 1.4393; d_4^{20} 0.8944. The structure of this chloro compound has been proved by us in a previous communication [11].

Reaction of the Grignard Reagent from 3-Chloro-2,4-dimethyl-1-pentene with 2,4-Dimethyl-3-pentanone.

Dry 2,4-dimethyl-3-pentanone (17.2 g; b.p. 123°, n_D^{20} 1.4010) was added to iso-$C_7H_{13}MgCl$ prepared from 25 g of 3-chloro-2,4-dimethyl-1-pentene and 9.2 g of magnesium in 150 ml of absolute ether with vigorous mixing and very slow addition of the chloro compound. The reaction mixture was heated for four hours and then decomposed with 150 ml of ice water. The ether layer was separated and dried over calcined $CuSO_4$. After removal of ether and vacuum fractionation, 13.8 g of an alcohol was obtained. The reaction was repeated, 40.6 g of alcohol being obtained altogether.

A further fractionation at 3.5 mm yielded the following fractions:

Fraction I , b.p. up to 78.5°; 6.3 g; n_D^{20} 1.4595; d_4^{20} 0.8524
Fraction II, b.p. 78.5-80.5°; 30.5 g; n_D^{20} 1.4620; d_4^{20} 0.8614

Found MR 67.78
Calculated MR 67.91

Found %: C 78.97; 78.82; H 13.21; 13.25
$C_{14}H_{27}OH$. Calculated %: C 79.18 H 13.29

Ozonization of the Alcohol $C_{14}H_{27}OH$

A solution of 10 g of the alcohol in 55 ml of dry chloroform was ozonized with 4% ozone (6 liters per hour) for 15 hours. The ozonide was decomposed with 60 ml of 5% H_2O_2 with vigorous stirring, at first at room temperature, and then in a water bath for eight hours. The acids were neutralized with sodium carbonate. The aqueous layer was evaporated to dryness. The salts of the acids were decomposed with 20 ml of 20% H_2SO_4. The acids were extracted with ether and dried over calcined Na_2SO_4. The ether was driven off, and the acids were distilled at atmospheric pressure, yielding the fractions:

Fraction I , b.p. 97-138°; 0.55 g; n_D^{22} 1.3816
Fraction II, b.p. 138-150°; 1.0 g; n_D^{22} 1.3901

The residue was a small amount of resin. A content of 31 mg of formic acid was found in Fraction I by the calomel method. Fraction II was treated with 1.5 g of thionyl chloride at 90-95° for 30 minutes. The acid chloride was carefully introduced into 20 ml of 27% ammonia solution at −10°. Water was evaporated away at room temperature. A part of the solid residue was vacuum-sublimated: the melting point of the amide so obtained was 125-126°, that of the amide of authentic isobutyric acid was 127-128°, and that of a mixture of these preparations was 125-127°. The chloroform layer and the ether extracts from the aqueous layer after it had been treated with sodium carbonate were united and dried over calcined Na_2SO_4. The ether and chloroform were distilled off under atmospheric pressure, and the residue distilled under reduced pressure (4 mm), yielding the fractions:

Fraction I , b.p. up to 67°; 4.4 g; n_D^{21} 1.4494
Fraction II , b.p. 67-84°; 0.5 g; n_D^{21} 1.4525
Fraction III, b.p. 84-90°; 0.5 g; n_D^{21} 1.4614
Fraction IV, b.p. above 90° — a resin

Fraction I was redistilled at 8 mm Hg:

Fraction I, b.p. 57-60°; 2.2 g; n_D^{20} 1.4474; d_4^{20} 0.8618
Fraction II, b.p. 60-63°; 1.9 g; n_D^{20} 1.4505

MR for fraction of b.p. 57-60°: found 47.86, calculated for $C_{10}H_{18}O$, 47.95.

From the same fraction a semicarbazone was prepared; after two crystallizations from ethanol it melted at 195°.

Found %: C 63.10; 63.09; H 10.05; 9.85; N 20.37; 20.63

$C_{11}H_{21}N_3O$. Calculated %: C 62.52 H 10.02 N 19.89

Fraction III of the first fractionation, in which the ketone $C_{13}H_{26}O_2$ corresponding to the alcohol (IV) might be supposed to occur, gave an insignificant amount of semicarbazone, m.p. 192° (single crystallization from alcohol); its melting point in admixture with the semicarbazone from Fraction I was 192-193.5°.

Dehydration of the Alcohol $C_{14}H_{27}OH$

The alcohol (20.3 g) was mixed with 3 g of anhydrous $CuSO_4$ and heated for several hours at 150°, yielding 14 g of a diolefin, b.p. 76-78° (8 mm); d_4^{20} 0.7910; n_D^{20} 1.4527.

The diolefin was hydrogenated, first over platinized charcoal in presence of chloroplatinic acid, and then in an autoclave over nickel at 190-230° and 200-230 atm. The product, after the usual treatment and distillation over sodium, was 2,5,7-trimethyl-3-isopropyloctane, which has been previously synthesized by Petrov and Ponomarenko [11] by another method.*

Reaction of i-$C_7H_{13}MgCl$ with Amyl Butyrate

A solution of amyl butyrate (21 g) in 50 ml of absolute ether was added dropwise with stirring to i-$C_7H_{13}MgCl$ prepared from 35.5 g 3-chloro-2,4-dimethyl-1-pentene and 6.45 g of magnesium in 100 ml of absolute ether. The reaction mixture was heated for six hours in a water bath and was then decomposed with ice water. The ether solution of the reaction products, together with ether extracts, was dried over anhydrous Na_2SO_4. The ether was distilled off and the residue vacuum-fractionated, yielding 12.6 g (35.5%) of an alcohol, b.p. 142-144°/11 mm; d_4^{20} 0.8659; n_D^{20} 1.4712; calculated MR 85.92; found MR 86.04.

Found %: C 81.32; 81.34: H 12.71; 12.82

$C_{18}H_{33}OH$. Calculated %: C 81.13; H 12.86

Ozonization of the Alcohol $C_{18}H_{33}OH$

A solution of 8.8 g of the alcohol in 40 ml of dry chloroform was ozonized with 6% ozone (4 liters per hour) for 12 hours. The ozonide, in its chloroform solution, was then decomposed by treatment, accompanied by vigorous stirring, with 100 ml of 1% H_2O_2 for six hours at room temperature and six hours in a water bath. A further 4 ml of 25% H_2O_2 was then added, and the decomposition products were heated in a water bath for one hour further. The acids were neutralized with sodium carbonate, and the neutral products were extracted with ether. Analysis by the calomel method revealed the presence of 0.364 g of formic acid.

The neutral solution of salts was evaporated down, and the salts were decomposed with 20% H_2SO_4. The acids were extracted with ether, and the ether extracts were dried over anhydrous Na_2SO_4. The ether was distilled off, and the residue (0.6 g) treated with 1.5 g of thionyl chloride for 30 minutes at 90-95°, and then with a 22% solution of ammonia. The product was 70 mg of amide, which after several sublimations and drying over calcined $CaCl_2$ melted at 121-123°. The melting point of the amide of authentic isobutyric acid was 125-126°, and the mixed melting point was 124-125°. The neutral products were not analyzed.

Reaction of i-$C_7H_{13}MgCl$ with Ethyl Formate

Dry ethyl formate (9.8 g) was added slowly (dropwise) to i-$C_7H_{13}MgCl$ prepared from 35.5 g of 3-chloro-2,4-dimethyl-1-pentene and 6.45 g of magnesium in 120 ml of absolute ether. The temperature of the reaction mixture was maintained at about + 5°. The mixture was set aside for 30 hours, and a further 45 ml of dry ether was then added. The mixture was then heated for five hours, decomposition was effected with ice water, and the reaction products were extracted with ether. The ether extract was dried, and the ether was distilled off. The residue was distilled twice at 3 mm in a current of nitrogen, yielding 7.3 g (23%) of the formic ester of an alcohol of composition $C_{15}H_{27}OH$; b.p. 111-113° (3 mm); d_4^{20} 0.9099; n_D^{20} 1.4662; found MR 76.85; calculated MR 76.81.

Found %: C 76.04; 75.95; H 11.21; 11.18

$C_{16}H_{28}O_2$. Calculated %: C 76.14 H 11.18

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* We take the opportunity of correcting one of the constants of this hydrocarbon: n_D^{20} 1.4370, and not 1.4310 as stated.

Hydrolysis of the Ester $C_{16}H_{28}O_2$.

The ester was hydrolyzed with 11 g of KOH in 50 ml of methanol. The mixture was boiled in a water bath for 12 hours, and the hydrolysis mixture then mixed with a large amount of water. The upper layer was extracted with ether, and the ether was removed from the extract. The product was 3.2 g of an alcohol, b.p. 111-113° (9 mm); d_4^{20} 0.8719; n_D^{20} 1.4670; found MR 71.40; calculated MR 72.06.

Found %: C 80.09; 80.04; H 12.76; 12.52

$C_{15}H_{27}OH$. Calculated %: C 80.29; H 12.57

SUMMARY

1. The reactions of the Grignard reagent derived from the "sterically hindered" 3-chloro-2,4-dimethyl-1-pentene with 2,4-dimethyl-3-pentanone, ethyl formate, and amyl butyrate indicate the favorable effect of a double bond in the β-position on the synthesis of highly branched alcohols, which cannot be prepared by reaction with the corresponding saturated haloalkanes.

2. It has been shown that the Grignard reagent derived from 3-chloro-2,4-dimethyl-1-pentene differs fundamentally from 2-butenylmagnesium chloride in that its reaction with 2,4-dimethyl-3-pentanone gives as its main product the alcohol corresponding to the primary form of the alkenylmagnesium halide.

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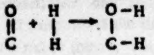
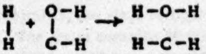
SEMICATALYTIC HYDROGENATION AND DEHYDRATIONAL CONDENSATION IN THE MECHANISM OF THE ISO SYNTHESIS

Ya. T. Eidus

The synthesis of hydrocarbons from carbon monoxide and hydrogen at normal or medium (10-15 atm) pressures is effected in presence of catalysts containing metals of Group VIII of the periodic system. The mechanism of the synthesis is most probably as follows [1]. Carbon monoxide and hydrogen molecules are activated at the catalyst surface and yield the unstable active group CHOH, formed in the first hydrogenation step from a CO molecule and an H_2 molecule. In the second hydrogenation step at the surface, the group CHOH reacts with a new H_2 molecule, forming a water molecule and a methylene group attached to the catalyst surface [2]:

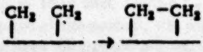


$$\begin{matrix}O\\ \|\\ C\end{matrix} + \begin{matrix}H\\ |\\ H\end{matrix} \longrightarrow \begin{matrix}O-H\\ |\\ C-H\end{matrix} \qquad (1)$$



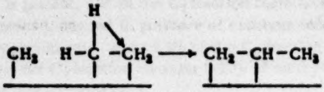
$$\begin{matrix}H\\ |\\ H\end{matrix} + \begin{matrix}O-H\\ |\\ C-H\end{matrix} \longrightarrow \begin{matrix}H-O-H\\ \\ H-C-H\end{matrix} \qquad (2)$$

This is succeeded by polymerization of methylene radicals at the surface of the catalyst. This process proceeds so that at first two methylene radicals combine to give an ethylene molecule adsorbed on two catalyst centers:



$$\underline{\begin{matrix}CH_2 & CH_2\\ | & |\end{matrix}} \rightarrow \underline{\begin{matrix}CH_2-CH_2\\ |\qquad |\end{matrix}} \qquad (3)$$

A new methylene group then unites to one of the two carbon atoms of the ethylene, and simultaneously an atom of hydrogen migrates and a methyl group is formed. As a result a molecule of propene is formed, and this also is attached to the catalyst surface at two centers.



$$\underline{\begin{matrix} & & H & \\ & & | & \\ CH_2 & H- & C & -CH_2\\ | & & | & |\end{matrix}} \longrightarrow \underline{\begin{matrix}CH_2-CH-CH_3\\ |\qquad\ |\end{matrix}} \qquad (4)$$

The process is continually repeated with the successive formation of molecules of butene, pentene, etc., also held on the surface by two atoms.

This mechanism of methylene radical polymerization is confirmed by the reaction of hydrocondensation of carbon monoxide with the simplest olefins [3]. Under certain conditions of synthesis, e.g., on iron catalysts, the water separating in the reaction of equation (2) participates in the water-gas reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2, \qquad (5)$$

and one of the final reaction products is, therefore, CO_2 [4]. It follows from the above discussion that the catalyst used in the synthesis has at least two functions: 1) to hydrogenate, and 2) to polymerize.

It is fairly often suggested in the literature that the fulfilling of the separate functions of a catalyst that is effecting a complex reaction is to be attributed to separate components of the catalyst [5]. Such differentiation of the action of catalyst with respect to its components is generally based on the properties of the isolated components. Such a point of view does not correspond altogether accurately to the actual state of affairs, inasmuch as the catalyst acts in all cases as a single whole and all qualitative and quantitative changes in its composition always affect all its functions in greater or less degree [6], but the notion nevertheless contains a certain amount of truth and enables us to consider the question of the effect of separate components of the catalyst on its various properties. Actually, separate functions of a catalyst can be strengthened or weakened, or even completely removed, while others are preserved. The addition, for example, of an alkaline agent increases the polymerizing action of a catalyst, and, as a result, the yield of high boiling fractions and solid paraffin is raised [5]. The hydrogenating propensity rises as we pass from iron catalysts to cobalt and further to nickel. Correspondingly, the content of unsaturated hydrocarbons in the gasoline fraction, b.p. up to 150°, falls from 80% to 31% and further to 12% [7]. These data show that the hydrogenating properties of the catalyst can be attributed to its main component, a metal of Group VIII. Similarly, the polymerizing effect is to be ascribed to difficultly reducible oxides: ThO_2, MnO, MgO, Al_2O_3, and others, which are present in the catalyst in small amount. To some of these, such as ThO_2 and Al_2O_3, a dehydrating effect is also ascribed, and this aids the elimination of water in the formation of CH_2 radicals [8].

The hydrogenating ability of a catalyst may be evaluated by carrying out the hydrogenation of olefin or aromatic hydrocarbons in its presence [6]. It follows from the above discussion that the hydrogenating component is essential for a synthesis catalyst. Until recently the only catalysts known for the practical synthesis of hydrocarbons from carbon monoxide and hydrogen contained Group VIII metals, Ni, Co, Fe, and Ru. Recently, however, the synthesis has been effected of hydrocarbons that are predominantly of the iso structure (iso synthesis) from carbon monoxide and hydrogen in presence of catalysts that do not contain any Group VIII metals, but consist only of zinc oxide or of difficultly reducible metal oxides, such as thorium, aluminum, and cerium oxides, taken separately or in pairs [9,5]. As an additive, an alkaline agent may be used [9,5]. The iso synthesis proceeds under the following optimum conditions: 450° at 300-600 atm; initial mixture approximately 1 CO : 1 H_2; space velocity for the passage of the mixture 500-1000 liters per liter of catalyst per hour. On ThO_2 at 450° and 600 atm the yield of products is 154 g per cubic meter; they include 18.2% of $CH_4 + C_2H_6$; 14.7% $C_3H_8 + n\text{-}C_4H_{10}$; 3.3% $(CH_3)_2O$; 29.3% of isobutane and isobutene, and 34.5% of liquid products.

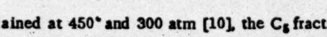
On the catalyst ThO_2-Al_2O_3 the yield of liquid products is 56 g per cubic meter, and the C_4 fraction amounts to 61 g per cubic meter. The latter contains 80-90% of hydrocarbons of iso structure. At pressures of more than 600 atm and temperatures below 400° a considerable amount of oxygen compounds is obtained; it consists mainly of methyl and isobutyl alcohols and dimethyl ether.

In the liquid product obtained at 450° and 300 atm [10], the C_5 fraction varies, according to the catalyst, from 5 to 27%, the C_6 fraction from 12 to 28%, and the C_7 fraction from 15 to 22%. The content of normal hydrocarbons is low. After hydrogenation of the product, the n-pentane content of the C_5 fraction is 11-19%; in the C_6 fraction the n-hexane content does not exceed 3-5.5%, whereas the 2-methylpentane content is 28-59%, the 2,3-dimethylbutane content is 11-41%, and the 3-methylpentane content is 10-16%; in the C_7 fraction, the sum of the amounts of 2- and 3-methylhexanes and 2,3-dimethylpentane comprises 28-44% of the fraction. In the iso synthesis, hydrocarbons having a tertiary carbon are also formed, although in small amounts. In the C_6 fraction 0.6-3.4% of neo-hexane is present, and in the C_7 fraction there is 0.4-12% of 2,2-dimethylpentane, and the greatest amount of such hydrocarbons is formed in presence of catalysts containing aluminum oxide. Products of the iso synthesis include also cycloalkanes: up to 1.2% of the C_5 fraction is cyclopentane, 2-15% of the C_6 fraction is methylcyclopentane, and the C_7 fraction contains 3-10% of methylcyclohexanes and 9-29% of dimethylcyclopentanes. The C_6 fraction contains also cyclohexane.

Two features of the iso synthesis deserve special attention from the theoretical point of view. First, the occurrence of the process in presence of catalysts that do not possess hydrogenation properties (Al_2O_3, ThO_2); second, the formation of hydrocarbons of iso structure. Let us examine these two peculiarities of the iso synthesis more closely and try to establish some relationship between them.

According to the most widely accepted modern theories of heterogeneous catalysis, particularly the multiplet theory [11], catalytic reactions proceed in the adsorbed layer. First of all, all the initial components of the reaction are activated when they are adsorbed on the surface; this may be expressed for the reaction

$$A + B \rightarrow C \qquad (6)$$

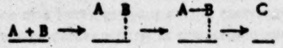


(7)

Consequently, the hydrogenating ability of a catalyst with respect, for example, to olefins is conditioned in the first place by its having the property of activating hydrogen molecules, as well as olefins molecules, when they come into contact with the surface. The absence of such hydrogenating ability may result from the impossibility of the activation of hydrogen molecules, or of olefin molecules, or of both simultaneously. It is well known that aluminum oxide is active in the reactions of the simplest olefins — for example, in hydration reactions.

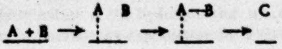
It may be assumed, however, with great confidence, that aluminum oxide and other such dehydrating catalysts for the iso synthesis are unable to activate hydrogen molecules; carbon monoxide molecules, on the contrary, are activated by these catalysts, a fact proved beyond doubt by the occurrence, under the conditions of the synthesis, of the Boudouard-Bell reaction [5].*

We may conclude from this discussion that in the iso synthesis in presence of Al_2O_3, ThO_2, and other catalysts the reaction proceeds without preliminary activation of hydrogen molecules by the catalyst, although it undoubtedly proceeds with the participation of hydrogen molecules. Hence, in spite of the demands made by the theories referred to above [11], a catalytic reaction may proceed in certain special cases without the activation on the catalyst of certain** of the initial components, which may therefore react with their partners on the catalyst without being in the adsorbed condition themselves. For the reaction of equation (6), this can be expressed by



(8)

or



(9)

The activation of such reaction components is, of course, of a purely thermal character. There are only a few references in the literature [12-15] to the possibility of the occurrence of hydrogenation in this way in other reactions. It was shown, however, in a study of the reactions of hydrogen containing deuterium in presence of catalytically active nickel [14] that at 20° and at 10 mm Hg the participation of ethylene in the reaction completely inhibited the para–ortho transformation of hydrogen, although hydrogenation occurred at zero order with respect to ethylene. The explanation advanced was that the nickel surface was, under these conditions, completely covered with ethylene, which prevented the adsorption and para–ortho transformation of hydrogen, but which was able to unite with hydrogen, possibly without the preliminary dissociation of this into atoms in the adsorbed layer.

Under the conditions of iso synthesis, the activation of hydrogen by the catalyst is evidently prevented not by the complete covering of the catalyst surface by carbon monoxide, but by the nature of the catalyst itself, and also, possibly, by the high temperature of the process. In this way there arises the idea of the possibility of the existence, in special cases, of "semicatalytic" reactions, which have as yet received very little study; the characteristic feature of such reactions is that some of the original reactants are activated by contact with the surface and remain bound to it during the reaction, and other reactants, on the contrary, are activated only thermally and may be in the gas phase during the reaction, although they will react with their reaction partners, which are attached to the catalyst.

According to the multiplet theory [11], in catalytic reactions only those atoms of the reactant molecules react that are directly bound to the catalyst surface. The reactant molecule must touch at least two active atoms of the surface, since the rupture of old, and formation of new, chemical bonds occurs between atoms that are attracted by different active atoms of the catalyst. The reaction center, therefore, coincides with a catalyst site. It is clear that, for the occurrence of a "semicatalytic" reaction, it is quite sufficient for the activated component attached to the catalyst to be linked to only one active atom of the surface.

Such activation of a molecule by contact with one active center does not always fix the place of reaction on the catalyst surface. Reaction with a molecule from the gas phase may occur both at the atom attached to the surface, and also with the atom not directly attached to the surface. In the latter case, the activation of the molecule attached to the catalyst through its bond with an atom of the catalyst and the effect of the latter on various atoms of the molecule attached to the catalyst find an analogy in that which in the chemistry of molecules is called "the mutual effect of atoms not directly linked together" [16]. Activation by contact therefore implies, not only molecular deformation and dynamic tension [17], but also the effect of the catalyst on the reactivity of atoms in the molecule attached to the catalyst. These two aspects are not in conflict, but are different manifestations of the same actuality – activation by contact. In a certain sense, Mendeleev was considering the chemical nature of interaction during catalysis when he wrote: "The degree, and even the period, of the perturbations or changes in movement will depend on the individual characters of the bodies coming into contact; i.e., will have a purely chemical character" [18].

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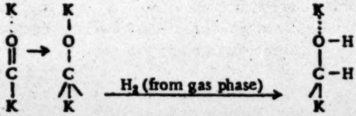
*The carbon formed by this reaction ($2CO \rightleftharpoons C + CO_2$) cannot initiate a hydrogenating function [17].

** But not all; otherwise the reaction would be not catalytic, but thermal.

"Semicatalysis" occupies an intermediate place between heterogeneous catalysis and homogeneous thermal reaction, inasmuch as the molecules of one reactant are activated by the catalyst, and the molecules of the other are activated thermally. It follows that semicatalytic reactions of this kind play an increasing part as the temperature of the chemical process rises, while not exceeding the temperature of the thermal reactions. Since the purely heterogeneous reaction goes, as is well known, with a lower activation energy than the corresponding thermal reaction, the activation energy for a semicatalytic reaction must be higher than for a purely heterogeneous reaction, but lower than for a thermal reaction.

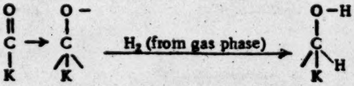
"Semicatalysis," as an intermediate form, is essentially distinct from other known transitional forms, such as catalysis in films on the surface of a heterogeneous carrier (heterogeneous ionic catalysis) [19], or homogeneous catalysis under the action of an active center arising at the surface and passing out further into the gas phase (heterogeneous—homogeneous catalysis) [20].

Returning to an examination of the first of the two peculiarities of the iso synthesis referred to above, we must acknowledge the semicatalytic nature of the hydrogenation processes in iso synthesis. The semicatalytic reaction must play an important part; it provides an explanation for a number of experimental facts. First of all, it is evidently to the semicatalytic hydrogenation that the extremely high temperature required in the iso synthesis must be attributed; this temperature, 450°, is much higher than those used for the usual syntheses over nickel, cobalt (180-210°), and even iron catalysts (200-350°). The high pressure also must be attributed to the same cause; this pressure (300-600 atm) is considerably higher than that required in the synol process (iron catalyst, 18-25 atm, 190-200°), the oxo synthesis (cobalt catalyst, 150-200 atm, 190-200°), the methanol process (zinc oxide, 130 atm, 400-450°), and the synthol process (alkaline iron oxide catalyst, 150 atm, 400-500°) [5]. Semicatalytic hydrogenation in the iso synthesis must effect important changes in the initial stages of the process. Whereas on catalysts containing Group VIII metals the carbon monoxide molecule rapidly passes, through two hydrogenation stages, via the CHOH group to the CH_2 radical according to equations (1) and (2) (above), on the nonhydrogenating catalyst of the iso synthesis the second stage of the hydrogenation may not occur for all of the CHOH groups, which in this case may be formed in two ways:



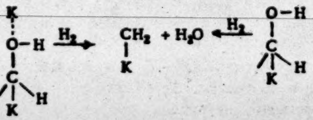
(10)

or



(11)

The difference between the CHOH groups in equations (10) and (11) is that in the first it touches two centers, and in the second, one; the position is the same for the original CO molecules. Slowness of hydrogenation may hold back the reaction at the first stage, with accumulation of appreciable amounts of CHOH groups at the catalyst surface, together with CH_2 groups. The latter are formed from CHOH groups as follows:

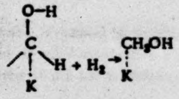


(12)

The accumulation of CHOH groups on the catalyst is of decisive significance for the further course of the reaction.

Let us consider the sort of transformation that the CHOH group can undergo. First, desorption from the surface accompanied by isomerization into formaldehyde: this process is not very probable. Then we may have semicatalytic hydrogenation with formation of a CH_2 group adsorbed on the surface; i.e., the reaction of Equation (12).

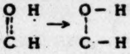
We must note further a special type of hydrogenation which the group CHOH can undergo and which does not occur when catalytic activation of hydrogen occurs, but only, evidently, by the semicatalytic method when the CHOH group is attached to only one active center (Equation 11). As a result of such a reaction a molecule of hydrogen is added with formation of methanol, which is one of the most important by-products of the iso synthesis:



(13)

It may be supposed that the processes of Equations 11 and 13, taken together, actually express the mechanism of the synthesis of methanol from CO and H_2 on ZnO and related catalysts.

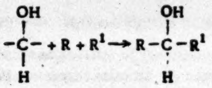
One of the most important of the other reactions that the CHOH groups may undergo is their copolymerization with CH_2 groups with formation of straight chains by reactions similar to those of Equations 3 and 4. Here we again meet a peculiar feature of the iso synthesis, as compared with the usual synthesis (in which the presence of CHOH groups in the carbon chain is exceptional, negligible amounts of oxygen compounds being formed). As early as 1946 we suggested the following scheme [3] to account for the formation of small amounts of propyl alcohol in the hydrocondensation of carbon monoxide with ethylene:

1) 

$$\begin{matrix} O & H \\ \| & \cdot \\ C & H \end{matrix} \rightarrow \begin{matrix} O - H \\ | \\ C - H \end{matrix}$$

2) $CH_2{=}CH_2 + CHOH \xrightarrow{+H_2} CH_3CH_2CH_2OH$ (14)

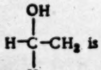
In the case of the iso synthesis, participation of CHOH groups in the formation of carbon chains is no longer the exception, but the rule. As they are bivalent, two groups R and R^1 will ultimately combine with them:



$$-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}- + R + R^1 \rightarrow R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R^1 \qquad (15)$$

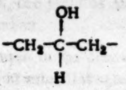
The following cases are possible:

1) If $R = H$ and $R^1 = H$, the final product will be methanol. This case has already been examined above.

2) If $R = H$ and $R^1 = CH_3$,  $H-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3$ is formed. (16)

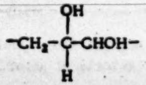
The final product after hydrogenation will be ethanol (or its higher homologs if $R^1 = CH_2{-}CH_2{-}CH_3$).

3) If $R = CH_2$ and $R^1 = CH_2$, the product will be



$$-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2- \qquad (17)$$

4) If $R = CH_2$ and $R^1 = CHOH$, the product will be



$$-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CHOH- \qquad (18)$$

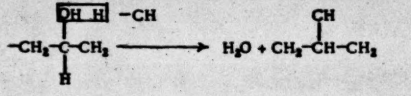
and so on.

All these groups may be more complex, since R and R^1 may be chains of methylene groups, and they may also contain CHOH groups. When we take into account the semicatalytic nature of the hydrogenation, i.e., the reaction of a complete H_2 molecule (from the gas phase), the addition of two hydrogen atoms at once to a CHOH group with formation of methanol is very probable, but addition of one hydrogen atom and one group containing a carbon atom

(Case 2) is less probable. The addition, however, of two organic groups is again very probable It follows that secondary hydroxyls will occur more frequently than primary hydroxyls in carbon chains, and this fact, as we shall see below, is of primary significance with respect to the final products of the iso synthesis. A primary hydroxyl will appear if one CHOH group unites with another CHOH. The intermediate groupings cited above may enter into further reactions.

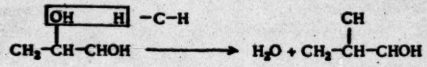
Until now polymerization by formation of new C—C bonds between CH_2 groups according to Equations 3 and 4 has been regarded as the only method by which hydrocarbon chains could be formed in the synthesis of hydrocarbons. This method undoubtedly applies also in the iso synthesis, but it is not the only method in this case.

If we consider the properties of the catalysts for this process, then it will be readily noted that they are distinguished not only by the absence of hydrogenating properties that could account for semicatalytic hydrogenation, but by powerful dehydrating effects (Al_2O_3, ThO_2, etc.), and therefore by dehydrational-condensation power. If, as we have seen, the first property is the cause of the formation of secondary hydroxyls in the carbon chains, then the second leads to the completion of the chains by condensation with elimination of water, and so to the inevitable formation of tertiary carbon atoms (cross condensation), with elimination of a hydroxyl of the chain and a hydrogen of a methylene group or, probably more rarely, a hydrogen of the chain and the hydroxyl of a CHOH group. The grouping 17, therefore, will give rise most simply and most frequently (by reaction with a methylene radical) to a species having the skeleton of isobutane, one of the main products of the iso synthesis:



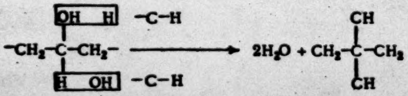
$$-CH_2-\underset{H}{\overset{\boxed{OH\ \ H}\ -CH}{C}}-CH_2 \longrightarrow H_2O + CH_2-\overset{CH}{C}H-CH_2 \qquad (19)$$

The skeleton of isobutyl alcohol, the most important oxygen compound in the iso synthesis, arises just as simply from the grouping 18 and a methlene radical:



$$CH_2-\overset{\boxed{OH\ \ \ \ H}\ -C-H}{C}H-CHOH \longrightarrow H_2O + CH_2-\overset{CH}{C}H-CHOH \qquad (20)$$

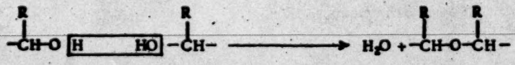
The grouping 19 may arise partially also by the condensation of the chain $-CH_2-CH_2-CH_2$ with a CHOH group, but at the same time addition may occur also at the terminal atom of the carbon chain. There is a certain probability also of the formation of chains containing a quaternary carbon atom: from grouping 17, one CH_2 group, and one CHOH group, the neopentane grouping can be obtained:



$$-CH_2-\underset{\boxed{H\ \ OH}\ -C-H}{\overset{\boxed{OH\ \ H}\ -C-H}{C}}-CH_2- \longrightarrow 2H_2O + CH_2-\underset{CH}{\overset{CH}{C}}-CH_2 \qquad (21)$$

Dehydrational condensation, as also semicatalytic hydrogenation, is slowed down by fall in temperature. Lowering the temperature to 375-400° at 300 atm therefore leads to the appearance of larger amounts of oxygen compounds, almost exclusively alcohols [21]. The yield of C_2-C_7 alcohols comprises 40-50% of the whole liquid product (apart from water) under these conditions, the yield of methanol varying from 15 to 30%, and that of isobutyl alcohol from 3 to 28% of liquid organic product.

Lowering of temperature must lead to increase in the concentration of CHOH groups and, consequently, of hydroxyl groups in the chains, and the formation of ether linkages becomes more probable:



$$-\overset{R}{C}H-O\boxed{H\ \ \ \ \ \ HO}-\overset{R}{C}H- \longrightarrow H_2O + -\overset{R}{C}H-O-\overset{R}{C}H- \qquad (22)$$

Actually, on a catalyst consisting of 80% ThO_2 + 20% Al_2O_3 at 375° and 300 atm the yield of dimethyl ether was 66 g / cu.m, the yield of liquid hydrocarbons being 12 g/ cu.m, of gaseous hydrocarbons 10 g/ cu.m, and of methanol 7 g/ cu.m [10].

It is very interesting to note that under these conditions the average content of olefins in the hydrocarbon fraction boiling up to 150° was 76-91%, whereas for the same catalyst and the same pressure, but at 425°, it was only 34% in the fraction boiling up to 195° (although it was 62% by weight for the narrow fraction boiling at 175°-195°). It will be seen, therefore, that with rise of reaction temperature the content of unsaturated hydrocarbons is reduced. It is found also that with rise in the boiling point of fractions of a given product the content of unsaturated hydrocarbons increases and there is a simultaneous fall in the content of branched hydrocarbons. All these relationships differ greatly from those observed in the usual synthesis, in which, on the contrary, rise in temperature leads to rise in the yield of unsaturated hydrocarbons, whereas, in a given product, the higher-boiling fractions are less unsaturated than the lower-boiling fractions.

All these facts are readily explained from the point of view developed above. In the usual synthesis, in which hydrogenation occurs by heterogeneous catalysis, rise in temperature favors increased dehydrogenation, resulting in an increased yield of unsaturated hydrocarbons. The higher-boiling fractions are desorbed after the lower-boiling fractions, and as a result they are more thoroughly hydrogenated. In the iso synthesis rise in temperature causes increased semicatalytic hydrogenation (a circumstance that is associated with the thermal activation of hydrogen), and this in its turn leads to an increased yield of saturated hydrocarbons. The above-mentioned relationship between the contents of olefins and of branched hydrocarbons in iso-synthesis fractions is extremely interesting: the higher the olefin content, the lower the content of iso compounds. The explanation of this may be as follows: in the long chains, dehydration at the expense of a hydroxyl and a hydrogen of a neighboring carbon atom predominates, and this leads to the formation of an olefin and also to the loss of the possibility of the formation of a side chain by cross condensation with CH_2 radicals; in short chains, on the other hand, dehydration is difficult, and this ultimately leads to dehydrational condensation with formation of a branched chain.

Increase in pressure up to 1000 atm acts in the opposite direction to increase in temperature: the result is an increased yield of oxygen compounds. Thus, over ThO_2 at 1000 atm and 400° the yield of $(CH_3)_2O$ alone was 200 g per cu.m. Under these conditions, evidently, we have almost exclusive hydrogenation of the CHOH group according to Equation 13, with subsequent ether formation according to Equation 22.

The great resemblance in the dependence of the nature of the final products on reaction temperature in the iso synthesis and the synol process [22] is worthy of note. The product of the synol process carried out at 190-200° under a pressure of 18-25 atm over Fe_2O_3 with additions of 2.5% Al_2O_3 and 0.5% K_2O contains about 50% of alcohols and 2-20% of esters. The remainder consists essentially of hydrocarbons. Over the same catalyst and at the same pressure, but at a higher temperature, 300-325°, the product consists mainly of hydrocarbons, with only 5-10% of alcohols. The iron catalyst of the synol process, unlike that of the iso synthesis, possesses hydrogenating powers, although they are considerably weaker than those of the cobalt and nickel catalysts of the usual synthesis. It is possible that, in addition to heterogeneous catalytic hydrogenation, semicatalytic hydrogenation occurs also in the synol process, which would explain the high yield of alcohols and its reduction with rise in temperature owing to increased hydrogenation on the one hand, and dehydration and dehydrational condensation on the other. There can be no doubt that the latter plays an important part in the formation of hydrocarbons of iso structure on iron catalysts, as also on the iso-synthesis catalysts, and no assumptions are necessary concerning the isomerizing properties of the two types of catalysts and the formation of branched hydrocarbons from primary hydrocarbon products of normal structure.

In just the same way, the assumption of the intermediate formation of alcohols in the iso synthesis, as made by the authors of the synthesis [21], is superfluous. These authors consider that formaldehyde is first formed from the mixture of CO and H_2, and this is further converted into methanol. Dimethyl ether is formed from methanol, and ethanol is formed from dimethyl ether. The interaction of ethanol and methanol yields isopropyl alcohol or ethyl methyl ether, which is further converted into propyl alcohol. Propyl alcohol reacts with methanol, yielding isobutyl alcohol, with ethanol, yielding 2-methyl-1-butanol, and with another molecule of propyl alcohol, yielding 2-methyl-1-pentanol. The whole of this scheme of conversions of alcohols into ethers, and these into alcohols having the same number of carbon atoms is unconvincing and does not explain the essential characteristics of the iso synthesis. We consider that the concept that we have expounded of a unified process leading, according to the conditions, to alcohols, ethers, or hydrocarbons, or to all these at the same time, is more natural and is nearer to the truth.

The conversion of dimethyl ether into hydrocarbons under the conditions of the iso synthesis [10] cannot serve as a proof of the contention of the authors of the iso synthesis, that it is an intermediate product in this synthesis [10, 2]. We may recall that it was found possible to obtain hydrocarbons from methanol, formic acid [22], and ketene [23] under the conditions of the usual synthesis over a cobalt catalyst; these results, however, did not mean that all these compounds are primary products of the synthesis.

SUMMARY

1. In the synthesis of hydrocarbons from carbon monoxide and hydrogen over nonhydrogenating oxide catalysts (Al_2O_3, ThO_2), which is called the iso synthesis, the hydrogenation processes are in the nature of semicatalytic reactions: carbon monoxide molecules are activated at the catalyst surface and are attached to the surface during the reaction, but the hydrogen molecules are thermally activated and react by moving from the gas phase, without becoming attached to the catalyst.

2. It has been suggested that semicatalytic reactions are not confined to the iso synthesis, but have a more general character.

3. In semicatalytic reactions, those atoms, in molecules attached to the catalyst, that enter the reaction must themselves be attached to the catalyst surface.

4. In the iso synthesis, CHOH groups, as well as CH_2 groups, take part in the formation of carbon chains.

5. Semicatalytic hydrogenation in the iso synthesis leads to increase in the concentration of CHOH groups and to the occurrence of hydroxyl groups at secondary carbon atoms in carbon chains.

6. Iso compounds are formed by catalytic condensation with elimination of water (dehydrational condensation).

7. The mechanism discussed readily explains the peculiar nature of the products and other experimental characteristics of the iso synthesis.

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HYDROGEN EXCHANGE BETWEEN SATURATED HYDROCARBONS AND SULFURIC ACID

D. N. Kursanov, V. N. Setkina, and O. D. Sterligov

The question of the reactivity of saturated compounds and of the relation of their reactivity to their chemical structure is a very important, but insufficiently studied topic of organic chemistry. The unsaturated hydrocarbons, constitute a particularly interesting object for investigation, for in the molecules of these substances the mutal effects of atoms are not complicated by additional effects due to hetero atoms and multiple bonds. One of the most interesting of the chemical reactions of hydrocarbons is the reaction of hydrogen-isotope exchange. Owing to the almost complete identity of the molecules of the initial and final substances, these reactions are the simplest reactions of hydrocarbons and are of particular significance for the formulation of theories of the reactivity of saturated organic compounds.

The tendency of hydrocarbons to undergo hydrogen exchange under the action of acids, particularly deuterium-enriched sulfuric acid, has not received systematic study until recently. Individual examples described in the literature lead to contradictory conclusions concerning the tendency of saturated hydrocarbons to under exchange [1]. This fact prompted us to carry out a systematic study of the tendency of hydrogen atoms in saturated organic compounds to undergo exchange under the action of acids. We have recently published a short paper [2], giving some of our results, and also a discussion of the mechanism of the hydrogen-exchange reactions of saturated hydrocarbons.

In the present paper a more detailed description is given of the results of our studies of the exchange reactivity of saturated hydrocarbons in presence of deuterium-rich sulfuric acid. These experiments were generally carried out under the following conditions: Heavy sulfuric acid (monohydrate), prepared by reaction of equimolecular amounts of sulfur trioxide and heavy water, was mixed with the hydrocarbon and shaken in a sealed tube at 20-25° in a shaker having a frequency of 150-180 per minute. At the end of the experiment the hydrocarbon was separated, freed from traces of sulfuric acid by washing with 30% aqueous caustic potash and distilled water, dried with potassium carbonate, and distilled over sodium.

It is interesting to note that in experiments with exchange-reactive hydrocarbons the sulfuric acid acquired a cherry-red or reddish-orange color, which largely disappeared on dilution with water; in some of the experiments with exchange-reactive hydrocarbons, the formation of small amounts of sulfur dioxide was observed. The distilled hydrocarbon was submitted to combustion over incandescent copper oxide in a current of dry air, and the density of the water obtained, after suitable purification, was determined by the flotation method [3].

The saturated hydrocarbons investigated for exchange reactivity had carbon skeletons of various types: hydrocarbons of normal structure (heptane and dodecane), hydrocarbons containing a tertiary carbon atom (3-methylpentane and 3-methylhexane), a hydrocarbon containing a quaternary carbon atom (2,2-dimethylhexane), and hydrocarbons containing both a tertiary and a quaternary carbon atom (2,2,3-trimethylbutane and 2,2,4-trimethylpentane).

All the hydrocarbons employed in our experiments were carefully purified by distillation through colums of 40-75 theoretical plates and passage through a layer of silica gel. The constants of the original hydrocarbons are given in Table 1.

TABLE 1

Hydrocarbon	B. p. (°C) (pressure in mm Hg)	n_D^{20}	d_4^{20}
Heptane	98.2-98.3 (760)	1.38766	0.6837
Dodecane	114.0-114.1 (27.5)	1.4221	0.7492
3-Methylpentane	63.4-63.5 (757)	1.37651	0.6644
3-Methylhexane	91.5 (745)	1.3887	0.6871
2,2-Dimethylhexane	105.8-106.0 (745)	1.3937	0.6953
2,2,3-Trimethylbutane	80.6-80.8 (760)	1.38921	0.6902
2,2,4-Trimethylpentane	99.1-99.5 (760)	1.3915	0.6931

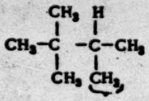
The results of our investigations are given in Table 2.

TABLE 2

Expt. No.	Hydrocarbon	No. of moles of acid	No. of moles of hydrocarbon	Duration of reaction (hrs)	Density excess of combustion water from hydrocarbon (γ) calculated* for 1 H		Density excess of combustion water from hydrocarbon (γ) calculated* for all H	found	Exchange (% of value calculated for exchange of all H)	
1	Heptane	0.045	0.023	1	—		3180	25	0.8	
2	Heptane	0.048	0.025	5	—		3069	34	1.1	
3	Heptane	0.050	0.018	10	—		4140	24	0.6	
4	Heptane	0.057	0.021	50	—		4112	70	1.7	
5	Dodecane	0.037	0.008	4	—		2346	28	1.2	
6	3-Methylpentane	0.052	0.017	5	806		4348	4206	96.8	
7	3-Methylpentane	0.059	0.017	10	957		5106	4945	96.9	
8	3-Methylhexane	0.052	0.022	11	799		3527	3392	96.2	
9	2,2-Dimethylhexane	0.051	0.029	4	—		3198	74	2.3	
10	2,2,3-Trimethylbutane	0.058	0.024	5	17042	for 7 H	22272	16410	96.3	of 7 H
11	2,2,3-Trimethylbutane	0.052	0.022	10	16616		21502	15170	91.3	
12	2,2,3-Trimethylbutane	0.044	0.020	25	15776		20116	20180	100	
13	2,2,4-Trimethylpentane	0.062	0.018	1	3454	for 9 H	4461	478	10.7	
14	2,2,4-Trimethylpentane	0.069	0.018	2	3420		4397	1293	29.4	
15	2,2,4-Trimethylpentane	0.070	0.021	3	3215		4085	1685	41.2	
16	2,2,4-Trimethylpentane	0.059	0.018	14	3185		4022	2463	60.0	
17	2,2,4-Trimethylpentane	0.035	0.017	12	14724		17443	14660	99.6	of 9 H
18	2,2,4-Trimethylpentane	0.047	0.020	25	16221		19604	18248	93.1	

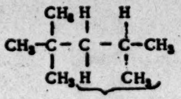
These results indicate the great difference in behavior of hydrocarbons of different structures. It will be seen from Table 2 that hydrocarbons whose molecules contain only primary, secondary, and quaternary carbon atoms practically do not enter into the hydrogen-exchange reaction (Expts. 1, 2, 3, 4, 5, and 9). On the other hand, hydrocarbons whose molecules contain a tertiary carbon atom (even if only one) show exchange reactivity, and it should be noted that all the hydrogen atoms of the molecule evidently take part in the exchange (Expts. 6, 7, and 8), and that exchange equilibrium is established extremely readily (in several hours at room temperature).

Hydrocarbons containing both tertiary and quaternary carbon atoms also take part in the exchange reaction and exchange all their hydrogen atoms for deuterium after a sufficiently long period. Under the conditions, however, under which 3-methylpentane and 3-methylhexane exchange all their hydrogen for deuterium (Expts. 6, 7, and 8), 2,2,3-trimethylbutane exchanges only 7 of its 16 hydrogen atoms for deuterium (Expts. 10 and 11), and 2,2,4-trimethylpentane exchanges 9 out of 18 hydrogen atoms; these results correspond to the exchange of all hydrogen atoms that occur in the molecule up to the quaternary carbon atom (Formulas 1 and 2):



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\;{-}\overset{\displaystyle H}{\underset{\displaystyle \underbrace{CH_3}_{7\,H},}{C}}{-}CH_3}$$

(1)



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}\underbrace{\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}}_{9\,H}{-}CH_3}$$

(2)

When the experiments are prolonged further all the hydrogen atoms of 2,2,3-trimethylbutane and 2,2,4-trimethylpentane are exchanged for deuterium (Expts. 12 and 18), and this is probably associated with the isomerization of the hydrocarbons under these conditions. The isomerization of hydrocarbons of this type in presence of concentrated sulfuric acid was studied recently by Komarewsky and Ruther [4]. An indirect confirmation of the occurrence of isomerization is afforded by the changes in the constants of 2,2,4-trimethylpentane when subjected to prolonged contact with sulfuric acid (see description of experiments).

When the present investigation had been completed, and simultaneously with the publication of our first communication [2], there appeared a paper by Stevenson, Wagner, Beeck, and Otvos in the Journal of American Chemical Society [5] which was also devoted to a study of the hydrogen exchange of saturated hydrocarbons under the action of sulfuric acid. The results obtained by these authors agree, in the main, with ours, and they confirm the high tendency for hydrogen atoms to undergo exchange in the molecules of saturated hydrocarbons containing one or more tertiary carbon atoms.

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* In the calculation the distribution coefficient was taken to be unity.

It must be pointed out that Stevenson, Wagner, Beeck, and Otvos differ from us in their conclusions regarding the number of hydrogen atoms taking part in the exchange reactions of hydrocarbons. They assert that all the hydrogen atoms take part in the exchange, with the exception of hydrogen atoms attached to tertiary carbons.

It should be noted that in the experiments of these authors the time of contact of the hydrocarbons with sulfuric acid was considerably shorter than in our experiments, and as a result the great majority of the molecules would succeed in assuming the ionic state on not more than one occasion. These conditions are essentially different from ours. The examples that we investigated do not permit us to make a completely unequivocal choice between the two possibilities indicated, because of the closeness of the density excess values calculated for exchange equilibrium with participation of all of the hydrogen atoms or of one less than this number. The question, therefore, of whether all of the hydrogen atoms of a hydrocarbon participate in exchange equilibrium, under the conditions of prolonged contact with sulfuric acid, requires further investigation.

EXPERIMENTAL*

1. Heptane and Heavy Sulfuric Acid

Heavy sulfuric acid was prepared from sulfur trioxide and water enriched in deuterium oxide. In this way samples of anhydrous sulfuric acid (containing in certain cases up to 2% of sulfur trioxide) having various equivalent density excesses were obtained. Heptane, b.p. 98.2-98.3°/ 760 mm, d_4^{20} 0.6837 and n_D^{20} 1.38766, was prepared from heptane of standard quality by washing with concentrated sulfuric acid, drying with calcium chloride, distillation through a 40-plate column, and final purification through a silica gel column.

A. A mixture of 2.30 g (0.023 mole) of heptane and 4.49 g (0.045 mole) of heavy sulfuric acid (equivalent density excess 17,000 γ) was shaken in a sealed tube in a shaker of frequency 150-180 per minute for one hour. The contents of the tube were separated in a separating funnel, and the hydrocarbon layer was washed with 30% aqueous caustic potash and with water It was then dried with potassium carbonate and distilled over sodium. The hydrocarbon was submitted to combustion over incandescent copper oxide, and the water produced was purified by our usual method [3]. The density excess of the water was determined by a densiometric method, the value obtained for the combustion water of heptane being 25 γ; the value calculated for the exchange of all 16 hydrogen atoms was 3180 γ.

B. A mixture of 2.51 g (0.025 mole) of heptane and 4.69 g (0.048 mole) of heavy sulfuric acid was agitated in a sealed tube for five hours. The contents of the tube were then treated as in Expt. A. The excess density of the combustion water of the heptane was found to be 34 γ, and the value calculated for full exchange of all of the hydrogen atoms was 3069 γ.

C. A mixture of 1.80 g (0.018 mole) of heptane and 4.95 g (0.050 mole) of heavy sulfuric acid was agitated for ten hours. The excess density of the combustion water of the heptane after the experiment was 24 γ, and the value calculated for full exchange of all of the hydrogen atoms was 4140 γ.

D. A mixture of 2.05 g (0.021 mole) of heptane and 5.59 g (0.057 mole) of heavy sulfuric acid was agitated for 50 hours. The value found for the excess density of the combustion water of the heptane was 70 γ, and the value calculated for the exchange of all of the hydrogen atoms was 4112 γ. The results of the experiments show that heptane practically does not undergo hydrogen exchange with sulfuric acid.

2. Dodecane and Heavy Sulfuric Acid

Dodecane was obtained from hexyl alcohol by converting it into hexyl bromide, and then by the Wurtz reaction into dodecane. The hydrocarbon was vacuum-distilled through a column of 75-80 theoretical plates, and it had the following constants: b.p. 114.0-114.1°/27.5 mm, d_4^{20} 0.7492; n_D^{20} 1.4221.

A mixture of 1.27 g (0.008 mole) of dodecane and 3.63 g (0.037 mole) of fuming heavy sulfuric acid (equiv. density excess 17,000 γ) was agitated in a sealed tube for four hours. After the experiment, the constants of the hydrocarbon were: b.p. 115-115.5°/ 32 mm, $n_D^{20.3}$ 1.4219; $d_4^{20.2}$ 0.7486. The density excess of the combustion water of dodecane was 28 γ, instead of the value required by calculation for the exchange of all of the hydrogen atoms, 2346 γ. These results show that under these conditions dodecane is not exchange reactive.

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* Laboratory worker A. N. Martynova assisted in the experimental work.

3. 3-Methylpentane and Heavy Sulfuric Acid

3-Methylpentane was prepared by hydrogenation in presence of a platinum catalyst [6] of the mixture of olefins obtained by the dehydration of 3-methyl-3-pentanol. It was distilled through a 40-plate column, and it had the following constants: b.p. 63.4-63.5°/ 757 mm, n_D^{20} 1.37651, and d_4^{20} 0.6644.

A. A mixture of 1.60 g (0.017 mole) of 3-methylpentane and 5.08 g (0.052 mole) of heavy sulfuric acid (equiv. density excess 15,350 γ) was agitated for five hours. After the experiment the constants of the hydrocarbon were: b.p. 60.5-61.5°/ 756 mm; n_D^{20} 1.3748; d_4^{20} 0.6638. The changes in the constants indicate that partial isomerization of the 3-methylpentane had occurred. The density excess found for the combustion water from 3-methylpentane was 4206 γ, and the calculated value for exchange of all hydrogen atoms was 4348 γ.

B. A mixture of 1.45 g (0.017 mole) of 3-methylpentane and 5.79 g (0.059 mole) of heavy sulfuric acid (15,350 γ) was agitated in a sealed tube for ten hours. After the experiment the constants of the hydrocarbon were: n_D^{20} 1.3742 and d_4^{20} 0.6640. The combustion water from the hydrocarbon had an excess density of 4945 γ, the value calculated for exchange of all hydrogen atoms being 5106 γ. The two experiments show that 3-methylpentane undergoes hydrogen exchange with sulfuric acid.

4. 3-Methylhexane and Heavy Sulfuric Acid

3-Methylhexane was prepared as follows. 3-Methyl-3-hexanol was prepared from 2-butanone and propyl bromide by the Grignard reaction, and was then dehydrated to give 3-methylhexene. This substance was hydrogenated at atmospheric pressure and room temperature in presence of platinized charcoal activated with chloroplatinic acid [6]. The 3-methylhexane was distilled through a 40-plate column; it had the following constants: b.p. 91.5°/ 745 mm; n_D^{20} 1.3887; d_4^{20} 0.6871.

A. A mixture of 2.20 g (0.022 mole) of 3-methylhexane and 5.10 g (0.052 mole) of fuming heavy sulfuric acid (15,500 γ) was agitated in a sealed tube for 11 hours. After the experiment the hydrocarbon was purified in the usual way; it had the following constants:b.p. 89.5-90°/749 mm; n_D^{20} 1.3881; d_4^{20} 0.6883. The excess density of the combustion water from the 3-methylhexane was 3392 γ, instead of 3527 γ required for exchange of all hydrogen atoms.

B. A mixture of 4.14 g (0.041 mole) of 3-methylhexane and 4.36 g (0.044 mole) of heavy sulfuric acid (110,520 γ) was heated in a sealed tube at 119-120° for 23 hours. The density excess of the combustion water from the hydrocarbon was 3600 γ instead of 12,850 γ, as required by calculation for exchange of all hydrogen atoms. These results indicate that 3-methylhexane is exchange reactive.

5. 2,2-Dimethylhexane and Heavy Sulfuric Acid

2,2-Dimethylhexane was prepared as follows. The Grignard reaction with tert-butylmagnesium chloride and butyraldehyde yielded 2,2-dimethyl-3-hexanol, which was acetylated with acetyl chloride in presence of barium carbonate. The acetate obtained was subjected to pyrolysis at 450°. The 2,2-dimethyl-3-hexene isolated from the pyrolysis products was hydrogenated in presence of a platinum catalyst [6]. The 2,2-dimethylhexane was distilled through a 40-plate column; it had the constants: b.p. 105.8-106.0°/ 745 mm; d_4^{20} 0.6953; n_D^{20} 1.3937.

A. A mixture of 3.25 g (0.029 mole) of 2,2-dimethylhexane and 5.85 g (0.051 mole) of heavy sulfuric acid (17,000 γ) was agitated for four hours. After the experiment the constants of the hydrocarbon were: b.p. 105.5°/ 745.5 mm; n_D^{20} 1.3937; d_4^{20} 0.6953. The value found for the density excess of its combustion water was 74 γ, and the value calculated for exchange of all hydrogen atoms was 3198 γ.

B. A mixture of 3.45 g (0.030 mole) of 2,2-dimethylhexane and 6.74 g (0.067 mole) of heavy sulfuric acid (92,000 γ) was heated in a sealed tube for five hours at 130° and 17.5 hours at 145-150°. After the experiment the hydrocarbon was purified in the usual way. The density of the combustion water from the 2,2-dimethylhexane corresponded to that of standard water. It follows from these experiments that 2,2-dimethylhexane, which has no tertiary carbon atoms, also has no exchange reactivity.

6. 2,2,3-Trimethylbutane and Heavy Sulfuric Acid

2,2,3-Trimethylbutane was prepared as follows. Pinacolone and methyl bromide were converted by the Grignard reaction into 1,1,2,2-tetramethylpropanol, which was dehydrated to give 2,2,3-trimethyl-3-butene. This substance was then hydrogenated under pressure at 160-170° in presence of a nickel catalyst, and the 2,2,3-trimethylbutane obtained was distilled and purified by passage through a silica gel column. The constants of the 2,2,3-trimethylbutane were: b.p. 80.6-80.8°/ 760 mm; d_4^{20} 0.6902; n_D^{20} 1.38921.

A. A mixture of 2.35 g (0.024 mole) of 2,2,3-trimethylbutane and 5.82 g (0.058 mole) of heavy sulfuric acid (94,000 γ) was agitated for five hours. After the experiment the hydrocarbon was purified in the usual way and had the following constants: b.p. 79.5-80.5°/ 760 mm; d_4^{20} 0.7074; n_D^{20} 1.3882. The value found for the excess density of the combustion water from 2,2,3-trimethylbutane was 16,410 γ, and the value calculated for exchange of all hydrogen atoms was 22,272 γ, and for the exchange of 7 hydrogen atoms (the number occurring up to the barrier formed by the quaternary carbon atom) – 17,042 γ.

B. A mixture of 2.20 g (0.022 mole) of 2,2,3-trimethylbutane and 5.22 g (0.052 mole) of heavy sulfuric acid (94,000 γ) was agitated for ten hours. After the experiment the hydrocarbon had the following constants: d_4^{20} 0.7072; n_D^{20} 1.3883. The density excess of the combustion water from the hydrocarbon was 15,170 γ, and the value calculated for exchange of 7 hydrogen atoms was 16,616 γ, and for exchange of all hydrogen atoms – 21,502 γ.

C. A mixture of 2.02 g (0.020 mole) of 2,2,3-trimethylbutane and 4.40 g (0.044 mole) of heavy sulfuric acid (94,000 γ) was agitated for 25 hours. After the experiment the hydrocarbon had the following constants: b.p. 79.5-80°/ 760 mm; d_4^{20} 0.7114; n_D^{20} 1.3880. The density excess of the combustion water from the hydrocarbon was 20,180 γ, the calculated values being 15,776 γ for exchange of 7 hydrogen atoms and 20,116 γ for exchange of all hydrogen atoms. The experiments show that the first seven hydrogen atoms undergo exchange more readily than the remainder.

7. 2,2,4-Trimethylpentane and Heavy Sulfuric Acid

2,2,4-Trimethylpentane was prepared from "isooctane" of standard quality by distillation through a 40-plate column, followed by purification in a silica gel column. It had the constants: b.p. 99.6-99.7°/ 760 mm; d_4^{20} 0.6908; n_D^{20} 1.3914.

A. A mixture of 1.72 g (0.015 mole) of 2,2,4-trimethylpentane and 10.27 g (0.104 mole) of fuming heavy sulfuric acid (17,000 γ) was agitated for 2 hours 30 minutes. The hydrocarbon dissolved to an appreciable extent in the sulfuric acid, and the sulfuric acid layer acquired an intense reddish-orange coloration. The 2,2,4-trimethylpentane, after the usual purification treatment, was subjected to combustion, and the density excess of the combustion water was 7590 γ, the value calculated for exchange of all hydrogen atoms being 7390 γ.

B. A mixture of 2.04 g (0.018 mole) of 2,2,4-trimethylpentane (b.p. 99.1-99.5°/ 760 mm; d_4^{20} 0.6931; n_D^{20} 1.3915) and 6.10 g (0.062 mole) of heavy sulfuric acid (15,300 γ) was agitated for one hour. After the experiment the hydrocarbon had b.p. 98.5-99°; d_4^{20} 0.6923, n_D^{20} 1.3915 The density excess of the combustion water from the 2,2,4-trimethylpentane was 478 γ; the value calculated for exchange of 9 hydrogen atoms was 3454 γ, and for the exchange of all 18 atoms – 4461 γ.

C. A mixture of 2.09 g (0.018 mole) of 2,2,4-trimethylpentane and 6.67 g (0.069 mole) of heavy sulfuric acid was agitated for two hours. After the experiment the hydrocarbon had b.p. 97.5-100°/ 760 mm; d_4^{20} 0.6936; n_D^{20} 1.3913. The density excess of the combustion water from the 2,2,4-trimethylpentane was 1293 γ; the value calculated for exchange of 9 hydrogen atoms was 3420 γ, and for the exchange of all hydrogen atoms – 4397 γ.

D. A mixture of 2.37 g (0.021 mole) of 2,2,4-trimethylpentane and 6.86 g (0.070 mole) of heavy sulfuric acid was agitated for three hours. After the experiment the hydrocarbon had b.p. 97-104°(760 mm); d_4^{20} 0.6914; n_D^{20} 1.3912. The density excess of the combusion water from the 2,2,4-trimethylpentane was 1685 γ; the value calculated for exchange of 9 hydrogen atoms was 3215 γ, and for all hydrogen atoms – 4085 γ.

E. A mixture of 2.03 g (0.018 mole) of 2,2,4-trimethylpentane and 5.79 g (0.059 mole) of heavy sulfuric acid was agitated for 14 hours. After the experiment the constants of the hydrocarbon were: 96.5-104°; d_4^{20} 0.6948; n_D^{20} 1.3937. The value found for the density excess of the combustion water from the hydrocarbon was 2463 γ; the value calculated for exchange of 9 hydrogen atoms was 3185 γ, and for exchange of all hydrogen atoms – 4022 γ.

F. A mixture of 1.94 g (0.017 mole) of 2,2,4-trimethylpentane and 3.49 g (0.035 mole) of heavy sulfuric acid (94,000 γ) was agitated for 12 hours. After the experiment the constants of the hydrocarbon were: b.p. 97-108°; d_4^{20} 0.7148; n_D^{20} 1.3954. The value found for the density excess of the combustion water was 14,660 γ; the value calculated for exchange of 9 hydrogen atoms was 14,724 γ, and for exchange of all 18 hydrogen atoms – 17,443 γ.

G. A mixture of 2.24 g (0.020 mole) of 2,2,4-trimethylpentane and 4.66 g (0.047 mole) of heavy sulfuric acid (94,000 γ) was agitated for 25 hours. After the experiment the constants of the hydrocarbon were: b.p. 97-115°; d_4^{20} 0.7225; n_D^{20} 1.3965. The density excess of the combustion water was 18,248 γ; the value calculated for exchange 9 hydrogen atoms was 16,221 γ, and for exchange of all hydrogen atoms – 19,604 γ.

On the basis of the experiments on exchange with 2,2,4-trimethylpentane, it follows that simultaneously with the exchange of hydrogen for deuterium atoms isomerization of the 2,2,4-trimethylpentane occurs. These results, as also the results of the preceding series of experiments, confirm that hydrogen atoms occurring on one side of a quaternary carbon (namely, the side containing the tertiary carbon) enter into the hydrogen exchange reaction more readily than the remaining hydrogen atoms.

We express our deep gratitude to A. L. Liberman for providing us with dodecane and 3-methylhexane required in our investigations, and to A. P. Meshcheryakov for providing 2,2,3-trimethylbutane.

SUMMARY

1. An investigation has been made into the exchange reactivity of the hydrogen atoms of saturated acyclic hydrocarbons under the action of sulfuric acid-d_2, the hydrocarbons studied being heptane, dodecane, 3-methylpentane, 3-methylhexane, 2,2-dimethylhexane, 2,2,3-trimethylbutane, and 2,2,4-trimethylpentane.

2. It has been established that only hydrocarbons containing a tertiary carbon atom enter into the exchange reaction with heavy sulfuric acid. For these hydrocarbons, exchange equilibrium is attained in a few hours at 20-25°.

3. It has been established that hydrogen atoms in saturated acyclic hydrocarbons containing tertiary carbon atoms have high mobility and are able to undergo exchange with deuterium in presence of heavy sulfuric acid.

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TRANSFORMATIONS OF VINYL ETHERS

SYNTHESIS OF HALO ACETALS FROM VINYL ETHERS

M. F. Shostakovsky and N. A. Gershtein

This paper describes the continuation of an investigation on the addition of chlorohydrins to alkyl vinyl ethers [1]. The reaction proceeds as follows:

$$CH_2{=}CH{-}OR + HOCH_2CH_2Cl \rightarrow CH_3CH(OR)OCH_2CH_2Cl.$$

The object of the investigation was a study of the effect of the nature of the halogen-substituted radicals in alkyl haloalkyl acetals on the tendency of these mixed acetals to undergo the disproportionation reaction that we have previously observed for mixed dialkyl acetals [2, 3]. The presence of halogen in these compounds may also be of interest for its own sake, since it makes it possible to pass to other series of compounds prepared by replacement of halogen by other functional groups [4].

The synthesis of alkyl 2-chloroethyl acetals has been developed and described by us previously, two examples being given [1]. We have now applied this method, which is extremely simple and may be carried out without the use of catalysts, to the synthesis of five new homologs Our starting materials were alkyl vinyl ethers and 2-chloroethanol. The alkyl vinyl ethers were prepared by Favorsky and Shostakovsky's method [5] and were purified by the method developed in our laboratory [6]. 2-Chloroethanol was purified by repeated distillation. Physical constants of the starting materials are given in Table 1.

TABLE 1

Physical Constants of Starting Materials

Formula of substance	B. p. (°C) (press in mm Hg)	d_4^{20}	n_D^{20}
$CH_2=CH-O-CH_3$	5 (744)	0.7725 (0°)	1.3730 (0°)
$CH_2=CH-OC_3H_7$	64-65 (760)	0.7678	1.3922
$CH_2=CH-OC_3H_7$-i	55-56 (760)	0.7518	1.3858
$CH_2=CH-OC_4H_9$-i	82-83 (760)	0.7680	1.3960
$CH_2=CH-OC_5H_{11}$-i	110-112 (760)	0.7822	1.4098
$HOCH_2CH_2Cl$	127.6-128 (760)	—	1.4407

EXPERIMENTAL*

The conditions of synthesis have been described in detail in the preceding communication [1]. In the case of methyl vinyl ether, some changes were necessary on account of its low boiling point (5°), and these are described below.

The synthesis of acetaldehyde 2-chloroethyl methyl acetal was carried out in a three-necked flask fitted with reflux condenser, mercury-sealed stirrer, and thermometer. 2-Chloroethanol (80 g, i.e., 1 mole) was introduced into the flask, which was cooled in an ice-salt bath to −8-10°, and methyl vinyl ether (58 g, i.e., 1 mole), previously cooled to the same temperature (the ampoule containing it was immersed in the same bath), was added in one lot through a side neck. The temperature of the reaction mixture rose rapdily to + 41°, and then soon began to fall. Stirring was continued for two hours, and the reaction mixture was then set aside overnight at room temperature. Vacuum fractionation of the reaction products yielded 80.5 g (61%) of acetaldehyde 2-chloroethyl methyl acetal, b.p. 52.0-52.9°/ 16 mm.

Details of the acetal syntheses are given in Table 2, and their physical constants are given in Table 3.

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*A. K. Gorban assisted in the experimental work.

TABLE 2

Details of Acetal Syntheses

Expt. No.	Formula of vinyl ether	Amount (moles)	Formula of alcohol	Amount (moles)	Formula of acetal		Yield (% on 2-chloroethanol)		
					Desired	Symmetrical	desired	symmetrical	total
1	$CH_2 = CH{-}O{-}CH_3$	1	$HOCH_2CH_2Cl$	1	$CH_3CH(OCH_3)OCH_2CH_2Cl$	$CH_3CH(OCH_3)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	61	9.6	70.6
2	$CH_2 = CH{-}OC_3H_7\text{-}n$	1.39	$HOCH_2CH_2Cl$	1.39	$CH_3CH(OC_3H_7\text{-}n)OCH_2CH_2Cl$	$CH_3CH(OC_3H_7\text{-}n)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	66.8	7.85	74.7
3	$CH_2 = CH{-}OC_3H_7\text{-}i$	1.5	$HOCH_2CH_2Cl$	1.5	$CH_3CH(OC_3H_7\text{-}i)OCH_2CH_2Cl$	$CH_3CH(OC_3H_7\text{-}i)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	64.8	10.02 15.70	90.52
4	$CH_2 = CH{-}OC_4H_9\text{-}i$	1	$HOCH_2CH_2Cl$	1	$CH_3CH(OC_4H_9\text{-}i)OCH_2CH_2Cl$	$CH_3CH(OC_4H_9\text{-}i)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	77.6	8.6	86.2
5	$CH_2 = CH{-}OC_5H_{11}$	0.23	$HOCH_2CH_2Cl$	0.23	$CH_3CH(OC_5H_{11}\text{-}i)OCH_2CH_2Cl$	$CH_3CH(OC_5H_{11}\text{-}i)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	93.2	–	93.2

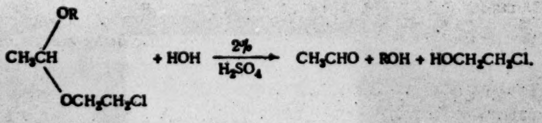
Note: In the synthesis of small amounts of material (Expt. 5) practically no disproportionation occurred. This is explained by the shorter period of heating during the distillation.

TABLE 3

Characteristics of Compounds Obtained

Formula of substance	B.p. (°C) (press. in mm Hg)	d_4^{20}	n_D^{20}	MR_D		Elementary analysis					
						C in %		H in %		Cl in %	
				Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$CH_3CH(OCH_3)OCH_2CH_2Cl$	52-52.9 (16)	1.0541	1.4211	33.35	33.44	43.21 42.95	43.33	8.11 8.04	8.00	25.76 25.5	25.58
$CH_3CH(OC_3H_7\text{-}n)OCH_2CH_2Cl$	55-57 (9)	0.9969	1.4232	42.79	42.68	50.93 51.07	50.45	9.53 9.18	9.07	21.26 21.20	21,28
$CH_3CH(OC_3H_7\text{-}i)OCH_2CH_2Cl$	42.5-44 (2)	0.9948	1.4218	42.55	42.68	50.40 50.36	50.45	8.84 8.96	9.07	20.96 21.10	21.28
$CH_3CH(OC_4H_9\text{-}i)OCH_2CH_2Cl$	68-69 (7)	0.9796	1.4245	47.11	47.30	53.42 53.18	53.18	9.08 9.17	9.48	19.09 19.01	19.63
$CH_3CH(OC_5H_{11}\text{-}i)OCH_2CH_2Cl$	60-63 (1.5)	0.9672	1.4312	52.12	51.92	55.61 55.67	55.52	9.92 9.96	9.84	18.29 18.42	18.21
$CH_3CH(OCH_2CH_2Cl)_2$	105.5-106 (12.5)	1.1793	1.4529	42.87	42.93	38.20 38.33	38.52	6.72 6.74	6.47	—	—
$CH_3CH(OC_3H_7\text{-}i)_2$	125.5-127.5 (360)	0.8158	1.3900	42.50	42.43	65.17 65.35	65.71	12.67 12.49	12.41	—	—

The structure of the acetals obtained was proved by hydrolysis with 2% sulfuric acid [7]. The reaction proceeds as follows:



$$CH_3CH\begin{matrix} OR \\ OCH_2CH_2Cl \end{matrix} + HOH \xrightarrow[H_2SO_4]{2\%} CH_3CHO + ROH + HOCH_2CH_2Cl.$$

The acetaldehyde formed was taken up with 0.2 N sodium bisulfite, the excess of which was titrated with 0.1 N iodine. Calculation was by the formula:

$$\% \text{ acetal} = \frac{K(a-b)M}{200w}$$

where K is the correction factor, a is the amount of iodine (ml) required in a control experiment, b is the amount of iodine (ml) used in the titration of the excess of bisulfite, M is the molecular weight of the acetal, and w is the amount of acetal taken. The hydrolysis results are given in Table 4.

TABLE 4

Hydrolysis of Acetals and Their Quantitative Determination in Terms of CH_3CHO

Formula of substance	Amount taken (g)	Amount of 0.1 N I_2 equiv. to bisulfite taken up	CH_3CHO found (% of theoretical)	Correction factor of 0.1 N I_2
$CH_3CH(OCH_3)OCH_2CH_2Cl$	0.1931	27.6	98	0.9899
	0.1529	22	98.7	
	0.1481	21.3	98.6	
$CH_3CH(OC_3H_7\text{-}n)OCH_2CH_2Cl$	0.1436	13.6	98	0.98692
	0.2358	17.3	99.1	
$CH_3CH(OC_3H_7\text{-}i)OCH_2CH_2Cl$	0.1976	23.85	99.3	0.98692
	0.2040	24.45	99.8	
$CH_3CH(OC_4H_9\text{-}i)OCH_2CH_2Cl$	0.2862	31.9	99.4	0.98692
	0.1328	14.8		
$CH_3CH(OC_5H_{11}\text{-}i)OCH_2CH_2Cl$	0.1316	13.6	99.3	0.98692
	0.1637	16.8	98.6	

SUMMARY

1. A study has been made of the addition of 2-chloroethanol to alkyl vinyl ethers.

2. It has been shown that the reaction is brought about in a very simple manner – by mixing equimolecular amounts of the components – and is accompanied by an exothermic effect.

3. Five new alkyl 2-chloroethyl acetals have been prepared: the 2-chloroethyl methyl, 2-chloroethyl propyl, 2-chloroethyl isopropyl, 2-chloroethyl isobutyl, and 2-chloroethyl isopentyl acetals of acetaldehyde.

4. These acetals, like other mixed acetals, are able to undergo disproportionation with formation of two symmetrical, dialkyl and bis(2-chloroethyl), acetals.

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* See Consultants Bureau Translation, p. 185.

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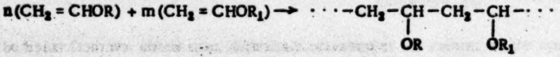
CHEMICAL REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 1. COPOLYMERIZATION OF METHACRYLIC ACID AND ALKYL VINYL ETHERS

M. F. Shostakovsky and A. M. Khomutov

Among the numerous methods of preparing macromolecular compounds, the copolymerization reaction occupies a special place. It is an extremely valuable synthetic method, permitting the preparation of macromolecular compounds having the most varied properties. In this reaction, various unsaturated compounds may be used as starting materials. By variation in the ratio of initial components and in the conditions of copolymerization, macromolecular compounds differing in composition, structure, and properties, can be obtained.

The simplest case of copolymerization is found when two unsaturated compounds react to form macromolecules having different alternating units:



$$n(CH_2=CHOR) + m(CH_2=CHOR_1) \rightarrow \cdots-CH_2-\underset{OR}{\underset{|}{C}}H-CH_2-\underset{OR_1}{\underset{|}{C}}H-\cdots \tag{I}$$

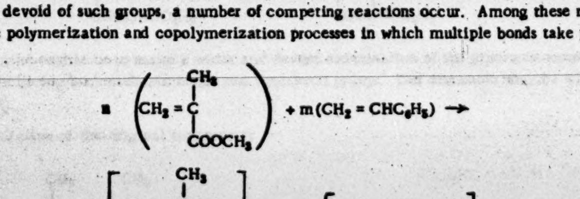
Copolymers of such regular structure, however, are exceptional.

Convincing proof of the above statements is to be found in the example of copolymerization of compounds of the same homologous series [1]. It was here established that the formation of the copolymer and its composition was determined by the activity of the initial monomers.

If due consideration is given to the method of copolymerization in the widest sense of the word, then we consider that the synthetic methods for the preparation of macromolecular compounds can be widened still further, if for this purpose not only multiple bonds are utilized, but also the functional groups of the starting substances, e.g. OH, COOH, NH_2, SH, etc. We have accordingly undertaken an investigation into the copolymerization of compounds of the following structures:

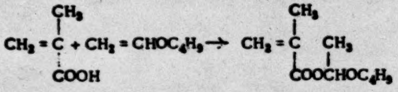
$CH_2=C(CH_3)COOH$; $CH_2=CHOAlk$; $CH_2=CHOAr$;
$CH_2=CHOCH_2CH_2NH_2$ [2]; $CH_2=CHOCH_2CH_2OH$ [3]; etc.

It is known from the literature [4, 5] that in the interaction of unsaturated compounds containing functional groups, or devoid of such groups, a number of competing reactions occur. Among these reactions, the most notable are polymerization and copolymerization processes in which multiple bonds take part [6]:



$$n\left(CH_2=\underset{COOCH_3}{\overset{CH_3}{C}}\right)+m(CH_2=CHC_6H_5)\rightarrow \cdots-\left[-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\right]_{n_1}-\left[-CH_2-\underset{C_6H_5}{CH}-\right]_{m_1}-\cdots \tag{II}$$

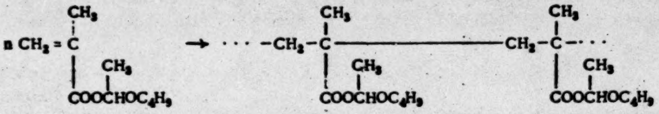
Among other forms of interaction between unsaturated compounds, we must refer to the reactions in which both multiple bonds and functional groups participate. In such cases the reactions may proceed in such a way that at first addition products are formed [7], e. g. 1-alkoxyethyl methacrylate:



$$CH_2=\underset{COOH}{\overset{CH_3}{C}} + CH_2=CHOC_4H_9 \rightarrow CH_2=\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}} \qquad \text{(III)}$$

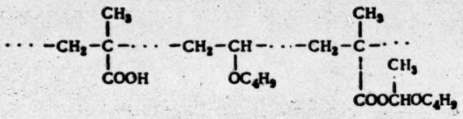
and then the following processes occur:

a) polymerization:



$$n\,CH_2=\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}} \rightarrow \cdots-CH_2-\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}}-\!-\!-\!-CH_2-\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}}-\cdots \qquad \text{(IV)}$$

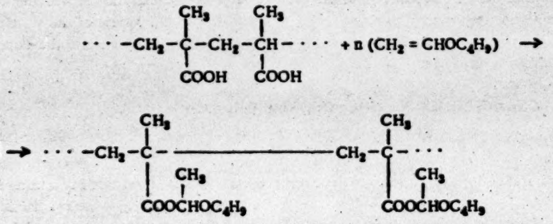
b) copolymerization of the original and newly formed compounds:



$$\cdots-CH_2-\underset{COOH}{\overset{CH_3}{C}}-\cdots-CH_2-\underset{OC_4H_9}{CH}-\cdots-CH_2-\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}}-\cdots \qquad \text{(V)}$$

It will be clear from the above that, with these reactions at our command, the synthetic methods available for effecting transformations of unsaturated compounds are greatly extended.

The synthesis of macromolecular compounds is therefore widened in scope by reactions in which not only multiple bonds, but also functional groups take part. This method enables us to prepare macromolecular products having a variety of structures. It can be applied not only to the original monomers, but also to macromolecular compounds, as illustrated by the example of polymethacrylic acid and an alkyl vinyl ether, when the reaction may proceed as follows:

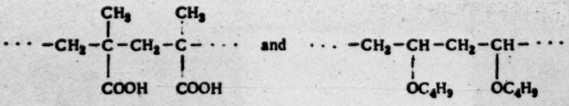


$$\cdots-CH_2-\underset{COOH}{\overset{CH_3}{C}}-CH_2-\underset{COOH}{\overset{CH_3}{CH}}-\cdots+n\,(CH_2=CHOC_4H_9) \rightarrow$$

$$\rightarrow \cdots-CH_2-\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}}-\!-\!-\!-CH_2-\underset{COO\overset{CH_3}{C}HOC_4H_9}{\overset{CH_3}{C}}-\cdots \qquad \text{(VI)}$$

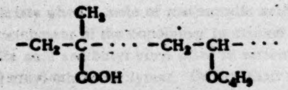
These examples enable us to make a wider and deeper examination of the processes occurring in the reactions of compounds having both multiple bonds and functional groups. Our discussion may be illustrated by the following schemes:

1) Polymerization of the original monomers:



$$\cdots-CH_2-\underset{COOH}{\overset{CH_3}{C}}-CH_2-\underset{COOH}{\overset{CH_3}{C}}-\cdots \quad \text{and} \quad \cdots-CH_2-\underset{OC_4H_9}{CH}-CH_2-\underset{OC_4H_9}{CH}-\cdots \qquad \text{(VII and VIII)}$$

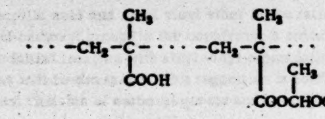
2) Copolymerization of the original monomers:



$$-CH_2-\overset{CH_3}{\underset{COOH}{C}}-\cdots-CH_2-\underset{OC_4H_9}{CH}-\cdots \qquad (IX)$$

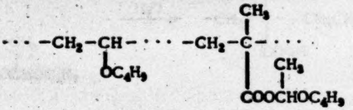
3) Formation of acylals, and their polymerization (III and IV).

4) Copolymerization of methacrylic acid with an acylal:



$$\cdots-CH_2-\overset{CH_3}{\underset{COOH}{C}}-\cdots-CH_2-\overset{CH_3}{\underset{COO\overset{CH_3}{CH}OC_4H_9}{C}}-\cdots \qquad (X)$$

5) Copolymerization of alkyl vinyl ether with an acylal:



$$\cdots-CH_2-\underset{OC_4H_9}{CH}-\cdots-CH_2-\overset{CH_3}{\underset{COO\overset{CH_3}{CH}OC_4H_9}{C}}-\cdots \qquad (XI)$$

6) Copolymerization of the original monomers and an acylal (V).

7) Addition of alkyl vinyl ether to a carboxyl group of the polymer or copolymer (VI).

The reaction of methacrylic acid with vinyl ethers is a convenient one for the preparation of macromolecular compounds having different contents of carboxyl groups.

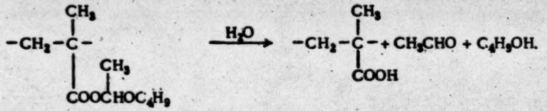
The composition and structure of copolymers of methacrylic acid with alkyl vinyl ethers (and also with acylals) were determined by elementary microanalysis, titration of free carboxyl groups, hydrolysis, and solubility determinations. The compositions of the copolymers are given in Table 1.

TABLE 1
Analytical Results for Copolymers

Monomers	Amounts (moles)	Content of		Acid and ether units in the copolymer		Fraction of possible carboxyls found (%)
		C (%)	H (%)	% by wt.	mole-%	
$CH_2=C(CH_3)COOH$	3	57.25	7.51	86.7	83.7	87.48
$CH_2=CHOC_2H_5$	1			13.3	16.3	
$CH_2=C(CH_3)COOH$	1	57.83	7.57	81.2	79.94	80.89
$CH_2=CHOC_2H_5$	1			18.8	20.06	
$CH_2=C(CH_3)COOH$	1	60.50	8.34	55.8	51.37	69.78
$CH_2=CHOC_2H_5$	3			44.2	48.63	
$CH_2=C(CH_3)COOH$	3	58.64	7.37	82.5	84.57	83.86
$CH_2=CHOC_4H_9$	1			17.5	15.43	
$CH_2=C(CH_3)COOH$	1	59.60	7.33	76.6	79.20	76.04
$CH_2=CHOC_4H_9$	1			23.4	20.80	
$CH_2=C(CH_3)COOH$	1	59.65	8.31	76.3	78.92	70.02
$CH_2=CHOC_4H_9$	3			23.7	21.08	

It will be seen from Table 1 that with increase in the amount of alkyl vinyl ether the carbon content of the copolymer increases. The dependence of the composition of the copolymer on the ratio of the original components is to be seen particularly clearly when 1 mole of methacrylic acid and 3 moles of ethyl vinyl ether are used in the reaction. In this case enrichment of the copolymer in alkoxyl groups occurs to the greatest extent. Copolymers formed from methacrylic acid and butyl vinyl ether in various proportions contain relatively fewer alkoxyl groups than the above ethyl vinyl ether copolymer. On this basis we may judge the differing activities of ethyl vinyl and butyl vinyl ethers. The same relation is to be found for the results for the methacrylic acid contents of the copolymer.

It follows from Table 1 that the results for the titration of carboxyl groups and the calculated composition of the copolymer from the elementary analysis are in satisfactory agreement. An exception is formed by copolymers obtained from methacrylic acid and alkyl vinyl ether in the ratio 1:3. This may be explained on the assumption that the number of carboxyl groups in the copolymer is reduced either owing to their addition to alkyl vinyl ethers, or owing to initial reaction with alkyl vinyl ethers followed by copolymerization as acylals: in both cases the final copolymers will be the same. This suggestion is confirmed by the fact that hydrolysis of these copolymers and subsequent titration of carboxyl groups and acetaldehyde gives results closely consistent with these views. The hydrolysis proceeds as follows [8]:



$$-CH_2-\overset{CH_3}{\underset{COOCH(CH_3)OC_4H_9}{C}}- \xrightarrow{H_2O} -CH_2-\overset{CH_3}{\underset{COOH}{C}}- + CH_3CHO + C_4H_9OH. \qquad (XII)$$

Determination of acetaldehyde iodometrically [9] gives the content of the corresponding vinyl ether in the original copolymer.

EXPERIMENTAL

The starting materials were methacrylic acid, ethyl vinyl ether, and butyl vinyl ether. Methacrylic acid having the following constants was used in all the experiments: b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0153; acid number 650 (mg KOH).

The vinyl ethers were prepared by Favorsky and Shostakovsky's method [10] and were purified by Shostakovsky and Prilezhaeva's method [11]. The ethyl vinyl ether used had the following constants: b.p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533. The butyl vinyl ether used had the following constants: b.p. 93.5-93.7°; n_D^{20} 1.4027; d_4^{20} 0.7791. Freshly distilled monomers were always used for the polymerization.

The polymerization was carried out in presence of benzoyl peroxide, which was purified by dissolution in chloroform, filtration, and precipitation with methanol [12]. The reprecipitation was repeated twice, after which further treatment with methanol was given and the material was dried in a vacuum desiccator until volatile substances (methanol) had been completely removed. The polymers and copolymers were dissolved in methanol having b.p. 64-65° and n_D^{20} 1.3300. Precipitation of the macromolecular substances obtained was effected with benzene of b.p. 80-80.5° and n_D^{20} 1.5010.

Experimental Procedure. The conditions for the copolymerization of methacrylic acid and alkyl vinyl ethers were investigated in sealed glass tubes, which were heated at 60 ± 1° in a thermostat until highly viscous or solid polymers were formed. In order to determine the activity of the benzoyl peroxide and the tendency of the original components to undergo polymerization, control experiments were carried out with methacrylic acid and the alkyl vinyl ethers separately.

The copolymerization of methacrylic acid with alkyl vinyl ethers was carried out in various molar ratios. The amount of benzoyl peroxide was 0.2% of the total weight of monomers. It was further necessary to determine the solubilities of the macromolecular compounds obtained in water, methanol, benzene, acetone, and ether. The polymers and copolymers were precipitated from solution with a 30-fold volume of precipitant. After separation of the macromolecular compounds, the mixture was distilled and the weight and composition of the residue were determined.

The presence of the original monomers in the polymers and copolymers was checked by extracting them with benzene and then estimating the multiple bonds in the extract with the aid of an aqueous solution of bromine

[13]. The polymer or copolymer was then dried, ground, extracted in the cold with benzene, and again dried. The polymers were dried in a vacuum drier at 45-50°, first at 15-20 mm, and then at 3 mm.

In order to calculate the yields of macromolecular compounds, drying was performed accurately within ± 0.01 g; for microanalysis the samples were dried to constant weight accurate within ± 0.0001 g. After being dried, the polymer and copolymer samples were stored in a vacuum desiccator over freshly calcined calcium chloride.

The separation of copolymers from polymers was effected by the method of selective dissolution. The elementary analysis was performed by micro methods. Carboxyl groups were determined in copolymers by titration. An excess of titration alkali was run into the polymer or copolymer solution, and the mixture was heated for 3-4 hours; the excess of alkali was then titrated with acid [14]. The structures and compositions of the synthesized compounds were studied.

Control Investigations. In order to verify the ability of the monomers used to undergo free-radical polymerization, control experiments were always carried out.

1. A study of the behavior of methacrylic acid toward benzoyl peroxide was carried out by the above-described procedure. The duration of an experiment was about eight hours, i.e., until a solid polymer of methacrylic acid was obtained. This polymer dissolved in cold water, in hot water, and in methanol. Titration revealed the presence in the polymer of 95.5% free carboxyl groups.

2. The behavior of benzoyl peroxide toward the alkyl vinyl ethers was carried out by the above-described procedure. The sealed tubes containing the alkyl vinyl ether and benzoyl peroxide were kept in the thermostat for 80 hours. The contents of the tubes were then distilled: the fractions obtained were found to be the original alkyl vinyl ethers, and a small amount of resinified material remained at the bottom; it was insufficient for quantitative investigation.

Copolymerization of Methacrylic Acid and Ethyl Vinyl Ether. For the copolymerization, 7.2 g of methacrylic acid and 17.8 g of ethyl vinyl ether were taken. The tubes were heated for 72 hours. The macromolecular compound formed was highly viscous. At the end of the reaction the tubes were cooled to 0°. The copolymerization conditions and the purification of the products are described above. The yield of copolymer was 10.75 g.

The copolymer obtained was ground, and its solubility in cold and hot water was studied. It was found that the water filtered from the copolymer contained no products having COOH groups; this was confirmed by titration in presence of phenolphthalein. The copolymer was soluble in methanol and ethanol, but insoluble in benzene and ether. The solutions of the copolymer in methanol were clear and viscous. In order to determine whether 1-ethoxyethyl methacrylate units were present in the copolymer chain, the material was titrated iodometrically. Some acetaldehyde was found, thus indicating the presence of 1-ethoxyethyl methacrylate units in the chain.

In addition, the copolymerization of methacrylic acid with ethyl vinyl ether was carried out with the following molar ratios of monomers (Table 2), other conditions being the same.

TABLE 2
Molar Ratios and Yields in Copolymerization of Methacrylic Acid and Ethyl Vinyl Ether

Molar ratio		Duration of polymerization (hr)	Yield of polymer (% on acid taken)	Appearance of polymer in tube before treatment
$CH_2=C(CH_3)COOH$	$CH_2=CH-OC_2H_5$			
1.0	–	7.5	90.2	White solid
0.75	0.25	7.0	105.4	White solid
0.50	0.50	80.0	120.0	Clear solid
0.25	0.75	72.0	150.0	Highly viscous, clear mass
–	1.0	80.0	–	Liquid

The copolymers produced from the monomers taken in various ratios were soluble in methanol and ethanol, but insoluble in benzene and ether. The differences in composition had a marked effect on the behavior of the copolymers toward water.

Copolymerization of Methacrylic Acid and Butyl Vinyl Ether. In this series of experiments, 5.56 g (1 molecular proportion) of methacrylic acid and 19.44 g (3 molecular proportions) of butyl vinyl ether were used. The duration of the polymerization was 72 hours. When the polymerization was complete, the tubes were cooled to 0°. The copolymerization conditions and the method of purification are described above. After reprecipitation of the copolymers, solvent and precipitant were distilled off under reduced pressure.

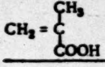
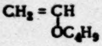
The following products were identified: solvent, precipitant, butyl vinyl ether, and methacrylic acid. A liquid having the specific odor of an acylal remained at the bottom of the distilling flask; p-toluylenediamine was added to the residue, and distillation was continued. As a result of the further distillation, an insignificant amount of liquid having n_D^{20} 1.4250 [7] was collected, and in addition some polymer remained in the flask. This was dissolved in acetone and then titrated iodometrically. The presence of 40.1% of ether groups was established. After being purified, the copolymer was dried; yield 7.65 g.

The ground copolymer was insoluble in cold and in boiling water. After being boiled with the copolymer, the water was filtered off, and was found to give a coloration with 0.05 N caustic soda in presence of phenolphthalein. The copolymer gave a gel in methanol and was insoluble in benzene.

Apart from this series of experiments on the copolymerization of methacrylic acid with butyl vinyl ether, other experiments were performed at other molar ratios. The same procedure was used for the copolymerization and the purification of the copolymers. The monomer ratios, yields, and other details are given in Table 3.

TABLE 3

Molar Ratios and Yields in Copolymerization of Methacrylic Acid and Butyl Vinyl Ether

Molar ratio		Duration of polymerization (hr)	Yield of polymer (% on acid taken)	Appearance of polymer in tube before treatment
 $CH_2=C(CH_3)COOH$	 $CH_2=CH-OC_4H_9$			
1.0	–	7.5	90.2	White solid
0.75	0.25	72	106.6	White solid
0.50	0.50	72	108.2	White solid
0.25	0.75	72	137.6	Clear solid
–	1.0	72	0	Liquid

The copolymers obtained with other monomer ratios were insoluble in benzene. The third copolymer (Table 3) gave a gel, insoluble in water, in the cold or at the boil.

The second copolymer (Table 3) gave a clear solution in methanol. In hot and in cold water these copolymers partially dissolve or swell.

SUMMARY

1. The conditions for the copolymerization of methacrylic acid with alkyl vinyl ethers have been investigated, and a number of new copolymers have been synthesized.

2. It has been shown that the copolymerization processes of unsaturated compounds in which there are functional groups having mobile hydrogen are accompanied by a number of side reactions.

3. It has been shown that acylals are formed in the course of the copolymerization process.

4. It has been established that screening of the carboxyl groups of the original methacrylic acid can be effected either by reaction of the methacrylic acid with alkyl vinyl ethers, or by copolymerization with the latter, or by addition of alkyl vinyl ethers to carboxyl groups of the copolymer.

5. It has been shown that, when suitable mixtures of methacrylic acid and alkyl vinyl ether react in presence of benzoyl peroxide, polymerization and copolymerization processes may predominate over side reactions.

6. In the course of investigations of the copolymerization of methacrylic acid and alkyl vinyl ethers, it has been shown that new copolymers, having hydrophilic (COOH) and hydrophobic (OR) groups, are formed.

7. It has been established that under these conditions alkyl vinyl ethers do not polymerize in presence of benzoyl chloride.

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IONIC POLYMERIZATION OF VINYL ETHERS

M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova

Vinyl ethers in presence of catalysts are converted into oily, highly viscous, or film-forming polymers. Suitable catalysts are halides [1], including hydrogen halides [2] and various salts: $SnCl_2$, $SnCl_4$, $AlCl_3$, etc. [3]. Boron trifluoride has been widely used abroad for this purpose, and Favorsky and Shostakovsky have introduced ferric chloride into scientific practice [3]: the polymerization of vinyl ethers is brought about by addition, in catalytic quantities, of an alcoholic solution of ferric chloride, the process being carried out at a temperature close to the boiling point of the monomer. Ethyl vinyl ether (b.p. 36°), for example, is polymerized at 35-41° [4], and butyl vinyl ether (b.p. 93-94°) at above 90° [5].

The ionic polymerization of vinyl ethers has been provided with a theoretical basis in Shostakovsky's oxonium theory [6]. The temperature is one of the principal factors determining the course of these processes in practice. The dissociation range of the oxonium complexes of a given alkyl vinyl ether corresponds approximately to the boiling point of the ether.

Descriptions of the preparation and properties of polymers of alkyl vinyl ethers are generally to be found in patent specifications, or they refer to isolated cases. In order to fill this notable gap, we have studied the polymerization of C_3-C_{12} alkyl vinyl ethers in presence of $FeCl_3$.

In the polymerization of vinyl ethers, the purity of the original monomers is of prime importance. The polymers and copolymers are of the highest molecular weight when they are obtained from ethers purified as follows: the crude ether is distilled, washed five times with water, dried with potassium carbonate, and distilled; it is finally treated with sodium and again distilled [7]. Aldehydes, ketones, alcohols, and other oxygen-containing compounds capable of forming peroxides retard polymerization [8]. Peroxides are formed also when alkyl vinyl ethers are kept: Shostakovsky and coworkers have established that freshly washed and distilled ethyl vinyl ether must be used for polymerization within three days [4].

Polymerization of alkyl vinyl ethers in presence of $FeCl_3$ generally proceeds at the boiling point of the monomers, or somewhat higher than this. This fact is explained by Shostakovsky by the decomposition of the vinyl ether-catalyst complex with formation of an active monomer molecule, which serves as an initiator of polymer chains.

Polymerization of vinyl ethers is carried out at ordinary pressure. About one-tenth of the monomer to be polymerized is placed in a flask and heated to the boil; ferric chloride (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) is then added dropwise, and the temperature rises spontaneously by 3-5°, and the macromolecular product is formed at the high rate that is characteristic for ionic reactions. Termination of chains occurs on account of the addition of $\bar{O}R$ or $\bar{O}H$, or the elimination of a proton, at the end unit [9].

Lowering of the temperature below that recommended leads to the formation of polymers and copolymers of low viscosity. The temperature is maintained at the required level by heating or addition of catalyst. It should be noted that for monomers having more complex molecules it is better to maintain the temperature at 5-10° above the boiling point of the ether. The polymerization of isopentyl vinyl ether (b.p. 111°), for example, goes well at 120°. The more severe conditions required for the polymerization of this ether are evidently related to its lower activity and to the high stability of its complex (vinyl ether $-FeCl_3$).

The polymerization of 200-300 g of monomer requires 3-4 hours, and at the end of this period the still-warm product is treated in a vacuum (12-18 mm) at 80-150° for 5-6 hours, i.e , until constant weight and refractive index is attained. The yield is 70-90% of the theoretical value: the polymer generally contains about 1% of monomer, which can be determined quantitatively, and about 15% of monomer is lost during polymerization and treatment under vacuum.

Polymers of C_3-C_7 vinyl ethers are colorless, highly viscous substances. C_8-C_{12} vinyl ethers also form macromolecular compounds, but they are colorless-yellow in varying degree, which is to be explained by partial destruction of the polymers in the process of formation (150-200°). For purification purposes the polymers are dissolved in benzene or ether. The solution is filtered, and the polymer is precipitated from the filtrate with water or an alcohol having a smaller radical than that of the original monomer. Dissolution and precipitation of polymer is repeated 2-3 times, until it is completely clarified. Finally, the product is placed under vacuum in a boiling water bath until constant weight and refractive index is attained. In the course of the reprecipitation there is naturally some loss of polymer, which reduces the yield.

The polymers are soluble in ether, benzene, acetone, chloroform, and other solvents. The polymers are soluble also in the alcohols from which the monomers are prepared, and in higher alcohols. The characteristics of the vinyl ether polymers are given in the table. In the molecular-weight determination we used the constant 0.000534, as established by the Vinyl Compound Laboratory of the Inst. Org. Chem., Acad. Sci. USSR.

It follows from the table that the molecular refraction rises in regular fashion. The viscosity of a 0.1 M solution rises with increase in length of the polymer chain. Polymers obtained from ethers of normal structure have higher molecular weights than those obtained from ethers having a radical of iso structure.

EXPERIMENTAL

1. Polymerization of Methyl Vinyl Ether

The amount of methyl vinyl ether (b.p. 5.5°, n_D^0 1.3730; d_4^0 0.7725 [10]) taken was 58 g (1 mole). About one-tenth of this was placed in a flask cooled with ice water and provided with a reflux condenser, and one drop of catalyst (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) was added. After 15-20 minutes vigorous boiling set in: part of the ether then evaporated, and the remainder polymerized into a slightly yellow, highly viscous substance. A fresh portion of the ether was added to the polymer obtained. Polymerization occurred after 10-15 minutes, and the resulting polymer was less viscous than that obtained with addition of catalyst. As further portions of the ether and the catalyst were added, the process went with spontaneous rise in temperature to 30°, reaction being less vigorous than in the formation of the first portion of polymer. The yield of crude polymer was 39.5 g (68%); n_D^{20} 1.4515. In order to remove monomer, the crude polymer was heated at 14-18 mm in a boiling water bath to constant weight (one hour). After the vacuum treatment the polymer had the following constants: n_D^{20} 1.4640; d_4^{20} 0.9423; absolute viscosity 0.7125 centipoise; relative viscosity 1.1107; specific viscosity 0.0788; M 2545; yield 30.6 g (52%).

Found %: C 62.13; 62.06; H 9.79; 9.52
C_3H_6O. Calculated %: C 62.04; H 10.41

The polymer of methyl vinyl ether slowly dissolves in cold water, but is again precipitated when the solution is warmed. It is soluble in methyl and other alcohols, and also in the usual organic solvents.

2. Polymerization of Propyl Vinyl Ether

The amount of propyl vinyl ether (b.p. 65.1°, n_D^{20} 1.3922; d_4^{20} 0.7678 [9]) taken was 86 g (1 mole). About one-tenth of this was placed in a three-necked flask provided with mercury-sealed stirrer, reflux condenser, and thermometer with its bulb at the bottom of the flask. Catalyst (two drops) was added to the boiling ether, and the temperature rose to 70°, the mixture becoming thick. The whole of the monomer was added over a period of one hour (five portions at ten-minute intervals). The optimum temperature for the polymerization of propyl vinyl ether is 65-70°, and it may be maintained in two ways: by placing the flask in a warm bath, or by addition of catalyst to the mixture. The yield of crude polymer was 77.5 g (90%); n_D^{20} 1.4468.

The crude polymer was dissolved in 300 ml of benzene, and the solution obtained was filtered. Methanol (200 ml) was then added to the filtrate in order to precipitate the polymer. The lower layer was separated, and the solvent was driven off. The polymer was exposed to a vacuum (13-18 mm) in a boiling water bath until constant weight was attained. The material purified in this way (62 g, i.e., 72%) had the following characteristics: n_D^{20} 1.4528; d_4^{20} 0.9368; absolute viscosity 0.8010 centipoise, relative viscosity 1.2382, specific viscosity 0.2218; M 4830. The polymer is soluble in propyl and higher alcohols, and in a wide range of other organic solvents.

Found %: C 69.91; 69.63; H 12.12; 12.11
$C_5H_{10}O$. Calculated %: C 69.72; H 11.70

3. Polymerization of Isopropyl Vinyl Ether

The amount of isopropyl vinyl ether (b.p. 55-55.6°, n_D^{20} 1.3861; d_4^{20} 0.7520 [9]) taken was 86 g (1 mole). The polymerization and treatment of the crude polymer were carried out as in Expt. 2. The pure polymer (60.3 g, i.e.,

TABLE

Characteristics of Vinyl Ether Polymers*

Name of polymer	Yield (%)	d_4^{20}	n_D^{20}	Viscosity of 0.1 M (calculated on monomer) benzene solution at 20° (centipoise)			M, calculated for monomer	Degree of polymerization
				Absolute	Relative	Specific		
Poly(methyl vinyl ether)	68	0.9423	1.4640	0.7185	1.1107	0.0788	58 2545	44
Poly(ethyl vinyl ether) [4]	79	0.9570	1.4520	0.8015	1.2389	0.2051	72 5334	74
Poly(propyl vinyl ether)	90	0.9368	1.4528	0.8010	1.2382	0.2218	86 4830	56
Poly(isopropyl vinyl ether)	61	0.9268	1.4520	0.7986	1.2345	0.2103	86 4580	53
Poly(butyl vinyl ether) [12]	92	0.9280	1.4570	0.8040	1.2420	0.2544	100 4738	47
Poly(isobutyl vinyl ether) [3]	90	0.9265	1.4565	0.7978	1.2333	0.2234	100 4183	42
Poly(isopentyl vinyl ether) [13]	86	0.9117	1.4607	0.7946	1.2129	0.2464	114 4048	36
Poly(hexyl vinyl ether)	89	0.9126	1.4632	0.8034	1.2419	0.2736	128 4003	31
Poly(cyclohexyl vinyl ether)	92	0.9364	1.4894	0.7357	1.1373	0.1040	126 1545	12
Poly(heptyl vinyl ether)	89	0.9132	1.4651	0.8255	1.2761	0.2350	142 3099	20
Poly(octyl vinyl ether) [14]	89	0.9230	1.4667	0.8534	1.3192	0.3550	156 4262	27
Poly(isooctyl vinyl ether)	93	0.9097	1.4664	0.8368	1.2905	0.2717	156 3261	21
Poly(nonyl vinyl ether)	87	0.9118	1.4676	0.8957	1.3846	0.3449	170 3799	22
Poly(decyl vinyl ether)	80	0.9282	1.4682	1.0105	1.5620	0.5174	184 5488	30

70%) had the following constants: n_D^{20} 1.4520; d_4^{20} 0.9268; absolute viscosity 0.7986 centipoise, relative viscosity 1.2345, specific viscosity 0.2103; M 4580. With respect to solubility the polymer of isopropyl vinyl ether was similar to that of propyl vinyl ether.

Found %: C 69.94; 69.71; H 11.95; 11.87
$C_5H_{10}O$. Calculated %: C 69.72; H 11.70

4. Polymerization of Hexyl Vinyl Ether

The amount of hexyl vinyl ether (b.p. 143.5°, n_D^{20} 1.4168; d_D^{20} 0.7970 [11]) taken was 128 g (1 mole). The polymerization was carried out as in Expt. 2. The optimum temperature for the process is 145-150°. The yield of crude polymer was 114 g (89%); n_D^{20} 1.4580. The crude polymer was dissolved in 500 ml of benzene, the solution was filtered, and the polymer was reprecipitated with 250 ml of ethanol. The alcohol and benzene were driven off, and the polymer was exposed to a vacuum (1 mm) in a boiling water bath until constant weight was attained (two hours). After purification the product (78.1 g, i.e., 61%) had the following characteristics: n_D^{20} 1.4632; d_4^{20} 0.9126; absolute viscosity 0.8034 centipoise, relative viscosity 1.2419, specific viscosity 0.2736; M 4003. The polymer of hexyl vinyl ether is soluble in hexyl and higher alcohols, and also in benzene, ether, and other organic solvents.

Found %: C 74.69; 74.85; H 12.70; 12.53
$C_8H_{16}O$. Calculated %: C 74.94; H 12.58

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*For all of the polymers the constants are ours.

5. Polymerization of Decyl Vinyl Ether

The amount of decyl vinyl ether (b.p. 224-225°, n_D^{20} 1.4347; d_4^{20} 0.8123 [11]) taken was 184 g (1 mole). The polymerization was carried out as in Expt. 2, the optimum temperature being 230-235°. The crude polymer was dissolved in benzene and precipitated with ethanol, and this reprecipitation operation was repeated twice The purified product (92.2 g, i.e., 50%) had the following constants: n_D^{20} 1.4682; d_4^{20} 0.9282; absolute viscosity 1.0105, relative viscosity 1.5620, specific viscosity 0.5174; M 5488. The polymer of decyl vinyl ether is soluble in decyl alcohol, benzene, and ether.

Found %: C 78.40; 78.49; H 12.75; 12.95
$C_{12}H_{24}O$. Calculated %: C 78.19; H 13.13

SUMMARY

1. The polymerization of C_8-C_{12} alkyl vinyl ethers had been studied.

2. The polymers obtained have been characterized with respect to viscosity, molecular weight, solubility, and elementary composition.

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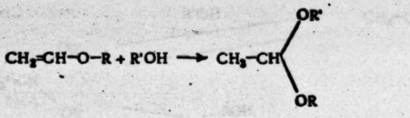
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 1. SYNTHESIS OF ACETYLENIC ACETALS FROM VINYL ETHERS AND ACETYLENIC ACLOHOLS

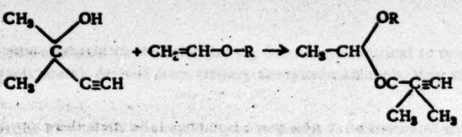
M. F. Shostakovsky and I. A. Shikhiev

At the present time the study of acetals derived from saturated and unsaturated alcohols presents great theoretical interest [1]. These compounds are highly reactive owing to the presence in them of a number of reaction centers. As the investigations of Shostakovsky and co-workers have shown [2], the simplest method of preparing acetals is by the addition of various alcohols to vinyl ethers in the manner indicated in the following equation:



(1)

The present investigation is concerned with the synthesis of acetylenic acetals, the formation of which may be represented by the following equation:



(2)

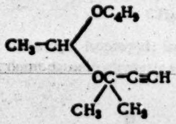
in which R = C_2H_5; $i\text{-}C_3H_7$ $i\text{-}C_4H_9$ C_4H_9

(I) (II) (III) (IV)

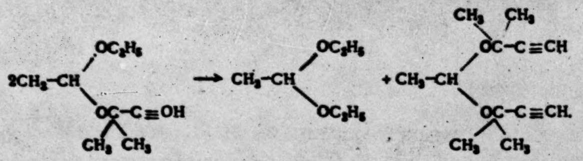
The addition of primary, secondary, and tertiary alcohols, and also of the corresponding unsaturated alcohols, to vinyl ethers, although performed by the same method in all cases, varies with respect to the experimental conditions required in the reaction.

We find, on passing from saturated alcohols (1) to unsaturated alcohols (2), that the acetals obtained are of still higher reactivity. The synthesis of acetals of the acetylenic series is best effected under mild conditions, i.e., in presence of catalyst at moderate temperature. The corresponding synthesis with heating in absence of catalyst is not applicable in this case [3].

In one of their papers Shostakovsky and Gershtein [4] have described the synthesis of an acetylenic acetal of the following structure:



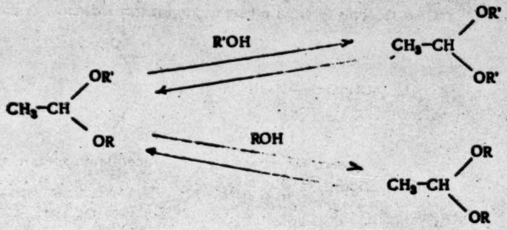
Since no disproportionation products were obtained in the course of the preparation of the acetal IV, it may be assumed that acetals of this series are not capable of disproportionation. We have, however, established that acetals derived from tertiary acetylenic alcohols undergo disproportionation to an extent that depends on the nature of the other alcohol residue. The disproportionation of mixed acetylenic acetals proceeds according to the equation:



(VI) (V)

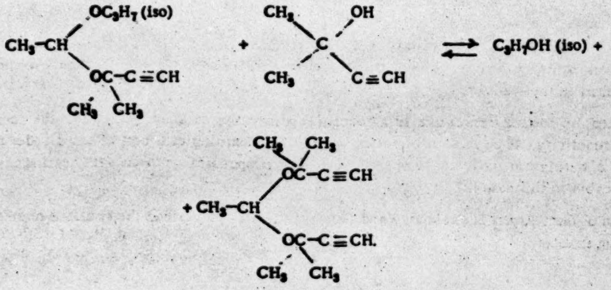
In the course of the synthesis of acetals of this series it was established that the tendency to undergo disproportionation falls off, according to the nature of the second residue, in the following order: $OCH_3 > OC_2H_5 > OC_3H_7 > OC_4H_9$. It may, therefore, be supposed that disproportionation depends to a certain extent on the size of the radical.

It is known [2, 5] that, under suitable conditions, saturated acetals undergo alcoholysis in an alcoholic medium according to the equations:

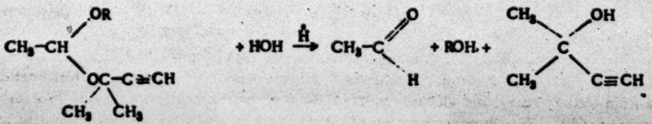


These equations indicate new synthetic methods for passing from unsymmetrical to symmetrical acetals, and in the reverse direction. As regards acetals derived from tertiary acetylenic alcohols, they also are able to undergo alcoholysis.

We have shown that the alcoholysis of acetaldehyde isopropyl 1,1-dimethyl-2-propynyl acetal in a medium of the acetylenic alcohol proceeds according to the equation:



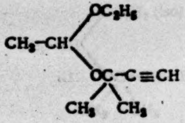
Altogether, we have prepared the ethyl, isopropyl, isobutyl, and butyl 1,1-dimethyl-2-propynyl acetals. Their structures were verified by breaking them down hydrolytically into their components as indicated in the equation:



EXPERIMENTAL*

The following starting materials were employed: 1,1-dimethyl-2-propyn-1-ol, b.p. 101-103°; n_D^{20} 1.4202; d_4^{20} 0.8578; ethyl vinyl ether, b.p. 36.0°; n_D^{20} 1.3776; d_4^{20} 0.7730; isopropyl vinyl ether, b.p. 55-55.5°; n_D^{20} 1.3860; d_4^{20} 0.7518; isobutyl vinyl ether, b.p. 83-83.5°; n_D^{20} 1.3986; d_4^{20} 0.7680; butyl vinyl ether, b.p. 93-94°; n_D^{20} 1.4020; d_4^{20} 0.7790.

1. Synthesis of the Ethyl 1,1-Dimethyl-2-propynyl Acetal I



A mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 72 g (1 mole) of ethyl vinyl ether was placed in a flask fitted with thermometer, condenser, and mechanical stirrer. The vinyl ether was taken in excess in order that no unchanged acetylenic alcohol should remain in the reaction mixture. Heating of the mixture for 18 hours at 80-90° did not result in acetal formation. When an addition of 0.02 ml of 30% hydrochloric acid was made to the mixture, the temperature rose to 57°. The mixture was set aside overnight, and on the next day the contents of the flask had become yellow. The reaction mixture was dried with potassium carbonate. The product (109 g) was vacuum-fractionated: unchanged starting materials were collected in a trap cooled to −16°, and the following fractions were collected:

Fraction I, b.p. 24-28° (12 mm); 4.6 g; n_D^{20} 1.4184
Fraction II, b.p. 42-43° (11-12 mm); 62 g; n_D^{20} 1.4162 (79.5%)
Undistilled residue 2,5 g

The contents of the trap (38 g) consisted essentially of unchanged ethyl vinyl ether containing traces of the acetylenic alcohol.

Investigation of Fraction II: d_4^{20} 0.8701; n_D^{20} 1.4162; found MR 45.01; calculated MR for $C_9H_{16}O_2 F^{\equiv}$ 45.046; found M 147.3; 149.0; calculated M 156.

Found %: C 69.55; 69.83; H 10.28; 10.27
$C_9H_{16}O_2$ Calculated %: C 69.23; H 10.25

These figures correspond to the unsymmetrical acetylenic acetal I. With ammoniacal silver nitrate Fraction II gave the white precipitate characteristic for monosubstituted acetylene compounds.

Hydrolysis of the Mixed Acetal I. A weighed amount of the acetal was placed in a flask, 25 ml of 2% sulfuric acid and 25 ml of 0.2 N sodium bisulfite were added, and the flask was shaken until the acetal had completely dissolved After 20 minutes the excess of sodium bisulfite was titrated with 0.1 N iodine.

Found: 98.36% and 94.4% of theoretical amount of acetaldehyde.

Distillation of the reaction product at atmospheric pressure yielded the following fractions:

Fraction I, b.p. 32-41°; 32 g; n_D^{20} 1.3789
Fraction II, b.p. 95-108°; 17 g; n_D^{20} 1.4088
Undistilled residue 58 g

Fraction I consisted essentially of ethyl vinyl ether. Fraction II was treated twice with sodium and, on being redistilled, yielded a fraction (6 g) of b.p. 102-104°, n_D^{20} 1.3800; d_4^{20} 0.8275, and a resinous residue (6.5 g). The fraction of b.p. 102-104° corresponded to the symmetrical diethyl acetal, for which the literature gives [6]: b.p. 103-104°; d_4^{20} 0.8254; n_D^{20} 1.3820.

The residue from the first distillation (58g) was vacuum-distilled, yielding a fraction of b.p. 36-38° (10-11 mm) (46 g; n_D^{20} 1.4168; d_4^{20} 0.8710) and a slightly colored residue (7 g). The constants of the fraction of b.p. 36-38° corresponded to the above-described unsymmetrical acetylenic acetal (I); it gave the characteristic white precipitate with ammoniacal silver nitrate.

The residue from the vacuum distillation (7 g), a slightly colored, oily liquid, was distilled in a current of nitrogen, and yielded the fractions:

Fraction I, b.p. 67-78° (2 mm); 1.2 g; n_D^{20} 1.4422
Fraction II, b.p. 79-82° (2 mm); 3.6 g; n_D^{20} 1.4468 Residue 2 g (resinous)

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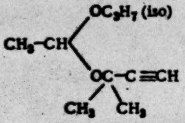
* Senior laboratory worker Z. S. Volkova assisted in the experimental work.

Fraction II gave a characteristic voluminous white precipitate with ammoniacal silver nitrate and had d_4^{20} 0.8076; n_D^{20} 1.4468; found MR 57.72; calculated for $C_{12}H_{18}O_2 |\!\equiv_2$ MR 56.898. According to its constants, Fraction II corresponded to the symmetrical diacetylenic acetal V. This acetal changed color on standing.

The discrepancies in the constants must be explained by the purification difficulties and the comparatively low stabilities of the acetals.

2. Synthesis of the Isopropyl 1,1-Dimethyl-2-propynyl Acetal II



Hydrochloric acid (0.02 ml) was added to a mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 86 g (1 mole) of isopropyl vinyl ether and the temperature of the reaction mixture rose to 78°. The mixture was set aside overnight, then dried with potassium carbonate, and finally vacuum-distilled through a trap cooled to −10-12°. The fractions obtained were:

Fraction I, b.p. 23-28° (11-12 mm); 9 g; n_D^{20} 1.3950
Fraction II, b.p. 47-48° (11-12 mm); (760 mm 153-55°); 65 g; n_D^{20} 1.4150 (76.5%)
Residue 2.3 g

The contents of the trap (47 g) consisted of isopropyl vinyl ether containing traces of 1,1-dimethyl-2-propyn-1-ol. Fraction I consisted essentially of isopropyl vinyl ether.

Investigation of Fraction II: d_4^{20} 0.8568; n_D^{20} 1.4150; found MR 49.57; calculated for $C_{10}H_{18}O_2 |\!\equiv$ MR 49.644; found M 158.5; 161.0; calculated M 170.

Found %: C 70.18; 70.39; H 10.12; 9.89
$C_{10}H_{18}O_2$. Calculated %: C 70.59 H 10.59

Fraction II gave the characteristic white precipitate with an aqueous-alcoholic ammoniacal solution of silver nitrate, and it corresponded in its constants with the isopropyl 1,1-dimethyl-2-propynyl acetal II. It should be noted that in the vacuum distillation no disproportionation of the acetal was observed, whereas in distillation at atmospheric pressure some decomposition occurred. The acetal II was hydrolyzed under the same conditions as in the preceding experiment:

Found: 99.87% and 99.62% of theoretical amount of acetaldehyde

Alcoholysis of the Isopropyl 1,1-Dimethyl-2-propynyl Acetal. A sealed tube containing 42.5 g (0.25 mole) of the acetal and 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol was heated in an oil bath at 170-180° for 52 hours, and the reaction products were then vacuum-distilled through a trap cooled to −12-16°, the following fractions being collected:

Fraction I, b.p. 19-21° (12 mm); 8.6 g; n_D^{20} 1.4063
Fraction II, b.p. 28-69° (12 mm); 20.7 g; n_D^{20} 1.4219
Fraction III, b.p. 70-78° (12 mm); 46.4 g; n_D^{20} 1.4533
Residue 4.5 g (resinous)

The contents of the trap (3 g) were added to Fraction I and, after two distillations, 4.2 g of a product of b.p. 81-83°, n_D^{20} 1.3812; d_4^{20} 0.7870. was isolated. These constants correspond to isopropyl alcohol, for which the literature [7] gives: n_D^{20} 1.37757; b.p. 82-83°.

Fraction II gave the characteristic white precipitate with ammoniacal silver nitrate. A second fractionation of this fraction yielded 16 g of a product of b.p. 101-103° and d_{20}^{20} 0.8578, which correspond to 1,1-dimethyl-2-propyn-1-ol [1].

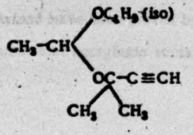
Fraction III was redistilled, when the greater part came over at 74-76° (12 mm), 32 g (33%) of a product corresponding to the symmetrical diacetylenic acetal V being obtained. Its constants were: n_D^{20} 1.4412; d_{20}^{20} 0.8967; found MR 57.15; calculated for $C_{12}H_{18}O_2 |\!\equiv_2$ MR 56.898.

Found %: C 74.12; 74.06; H 10.03; 10.12
$C_{12}H_{18}O_2$. Calculated %: C 74.22 H 9.27

The hydrolysis of the acetal obtained (V) was performed under the same conditions as in the preceding experiments:

Found: 98.39% and 98.10% of theoretical amount of acetaldehyde.

3. Synthesis of the Isobutyl 1,1-Dimethyl-2-propynyl Acetal III



The synthesis was performed under the same conditions as in the preceding experiments. Hydrochloric acid (0.02 ml) was added to a mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 100 g (1 mole) of isobutyl vinyl ether, and the temperature of the mixture then rose to 80°. The reaction product was dried with potassium carbonate and vacuum-distilled through a trap cooled to −10-12°, the following fractions being collected:

Fraction I, b.p. 20-32° (9-10 mm); 8 g; n_D^{20} 1.4010
Fraction II, b.p. 55-56° (9-10 mm); 72 g; n_D^{20} 1.4170
Residue 3.6 g

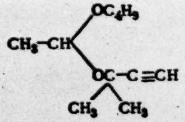
At atmospheric pressure the greater part of Fraction II came over at 173-174°. The yield was 78.26%. This fraction gave the white precipitate characteristic for monosubstituted acetylenes with aqueous-alcoholic ammoniacal silver nitrate, and it had the following constants: d_4^{20} 0.8587; n_D^{20} 1.4170; found MR 53.89; calculated for $C_{11}H_{20}O_2$ ⊨ MR 54.282.

Found %: C 71.55; 71.55; H 10.90; 10.90
$C_{11}H_{20}O_2$. Calculated %: C 71.73; H 10.87

These figures correspond to the acetal III. The contents of the trap (55 g) consisted essentially of isobutyl vinyl ether containing traces of 1,1-dimethyl-2-propyn-1-ol. Hydrolysis of the acetal III was effected as in the preceding experiments:

Found: 96.58% and 100.3% of theoretical amount of acetaldehyde.

4. Synthesis of the Butyl 1,1-Dimethyl-2-propynyl Acetal IV



The synthesis was performed as in the preceding experiment and yielded 75 g (81.52%) of a product having the following constants: b.p. 181-182° (760 mm); 62-63° (10-11 mm); n_D^{20} 1.4182; d_4^{20} 0.8592; found MR 53.99; calculated for $C_{11}H_{20}O_2$ ⊨ MR 54.282.

The product obtained (IV) gave the characteristic white precipitate with an aqueous-alcoholic ammoniacal solution of silver nitrate.

For the acetal IV the literature [3] gives: b.p. 181-182°; d_4^{20} 0.8579; n_D^{20} 1.4190.

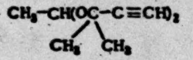
It should be noted that of the four unsymmetrical acetylenic acetals obtained, the butyl and isobutyl 1,1-dimethyl-2-propynyl acetals are the most stable when distilled. In this work we have shown also that the tertiary symmetrical unsaturated acetals V may be synthesized.

In the synthesis of the acetal I, disproportionation of the unsymmetrical acetylenic acetal was observed, the diethyl acetal VI and the diacetylenic acetal V being formed The structure of the acetal V is proved by its synthesis by the alcoholysis of the isopropyl 1,1-dimethyl-2-propynyl acetal II in a medium of 1,1-dimethyl-2-propyn-1-ol.

SUMMARY

1. The ethyl, isopropyl, isobutyl, and butyl 1,1-dimethyl-2-propynyl acetals of acetaldehyde have been prepared. The last has been described in the literature, but the first three are now synthesized for the first time.

2. The possibility of synthesizing the symmetrical acetylenic acetal



$$CH_3-CH(O\underset{CH_3\quad CH_3}{C}-C\equiv CH)_2$$

has been demonstrated for the first time.

3. The structures of the acetals obtained have been proved by hydrolytic breakdown into their components.

4. The disproportionation of unsymmetrical acetylenic acetals has been demonstrated for the first time.

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Institute of Organic Chemistry
of the USSR Academy of Sciences

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[7] G. Amkins and A. Wallach, J. Chem. Soc., 103, 1471 (1913).

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* See Consultants Bureau Translation, page 57.

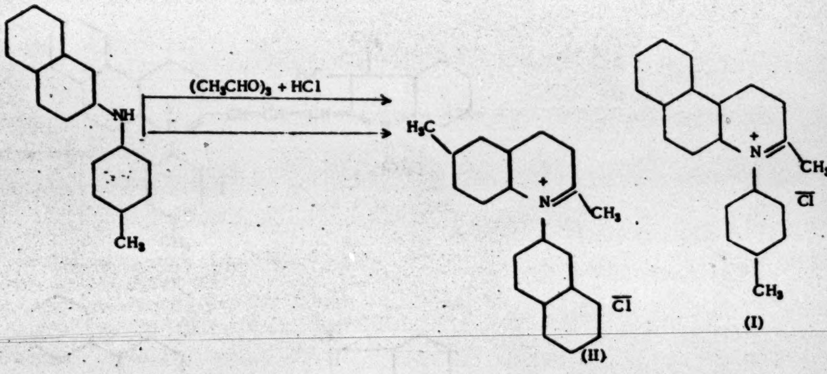
CYANINE DYES

COMMUNICATION 4. SYNTHESIS OF 3-METHYL-4-p-TOLYLBENZO[f]QUINOLINIUM IODIDE, AND SOME OF ITS REACTIONS

G. T. Pilyugin

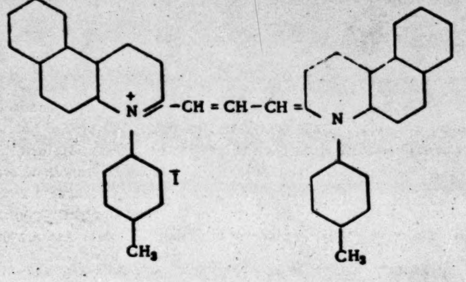
The preparation and reactions of quaternary salts of nitrogenous heterocyclic bases having aryl radicals on the hetero-nitrogen atom have received very little study. In 1936 Todd, Bergel, and Karimullah synthesized quaternary salts of the thiazole series arylated on the nitrogen by heating thioacetamides with chloroacetone [1]. Kiprianov and Ushenko have prepared quaternary salts having aryl radicals from benzothiazole derivatives [2]. 1-Arylquinolinium salts and their reactions are practically unknown. Pilyugin and Krainer prepared 2-methyl-1-phenylquinolinium perchlorate and converted it into carbocyanines of the quinoline series having phenyl on the hetero-nitrogen atom [3]; they showed that the introduction of phenyl in place of ethyl led to a bathochromic shift in the absorption maximum of 10 mμ.

We have prepared a number of arylated quaternary salts derived from quinoline and have shown that the cyclization of secondary aromatic amines in presence of paraldehyde and a small amount of an aromatic nitro compound in an acid medium is a general phenomenon [4]. The systematic investigation of this question is of undoubted scientific interest. We have condensed N-p-tolyl-2-naphthylamine with paraldehyde in presence of hydrochloric acid, a reaction that could proceed in two directions with formation of the isomeric quaternary salts shown below:



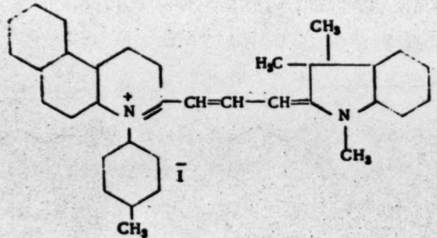
Experiment showed, however, that under our conditions the cyclization led in the direction of the formation of the 3-methyl-4-p-tolylbenzo[f]quinolinium salt (I). No other reaction products were detected. The salt was isolated in a microcrystalline form and had a relatively sharp melting point (185-186°), which indicated that it was homogeneous. The value of the absorption maximum (644 mμ) of the trimethinecyanine dye prepared from it confirmed its structure; if it had had the other structure, 2,6-dimethyl-1-(2-naphthyl)quinolinium salt (II), the absorption maximum of the dye would have been at a considerably shorter wavelength, for the analogous carbocyanine with a 1-naphthyl radical has an absorption maximum of 622 mμ [5]. The structure of the salt isolated is confirmed also by the fact that the absorption maximum of the dye obtained from the N-ethyl analog of this salt is 634 mμ [6].

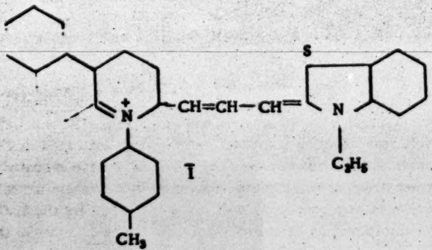
From the 3-methyl-4-p-tolylbenzo[f]quinolinium salts that we have synthesized for the first time we have prepared new cyanine dyes and have determined their absorption spectrum curves. Heating of the salt in pyridine with ethyl orthoformate yielded a dye of symmetrical structure, bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine iodide [7]



The absorption curve for this dye in ethanolic solution was determined on a spectrodensograph. Its absorption curve has two maxima at 644 and 595 mμ. The absorption maximum of this dye is displaced by 10 mμ toward the long waves with respect to that of its N-ethyl analog.

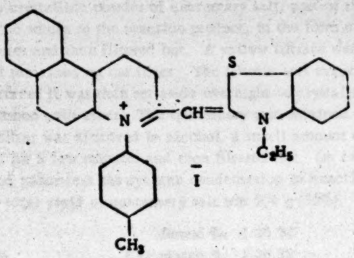
Condensation, in presence of pyridine and a few drops of acetic anhydride, of 3-methyl-4-p-tolylbenzo[f]-quinolinium iodide with 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)pseudoindolium iodide and with 3-ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide yielded unsymmetrical dyes [8]:





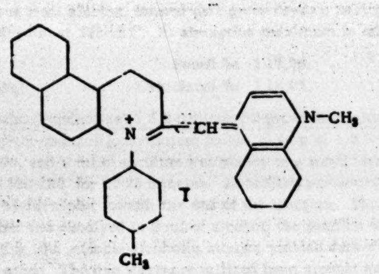
The absorption maxima of these unsymmetrical dyes are displaced from the additive value derived from the maxima of the corresponding symmetrical dyes in the direction of the ultraviolet, the first by 18.5 mμ, and the second by 5 mμ. The fused benzene ring at the *f* position in the quinoline nucleus displaces the absorption maxima of the unsymmetrical dyes by 4 and 8 mμ respectively with respect to the analogs without the fused benzene ring.

Condensation of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide with 3-ethyl-2-methylthiobenzothiazolium iodide yielded a dye of unsymmetrical structure, (4-p-tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine iodide:

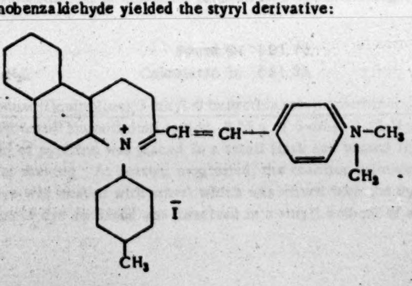


which has an absorption maximum at 495 mμ.

Heating of the quaternary salt with 1-methylquinolinium iodide in presence of caustic potash and sodium ethoxide yielded a monomethinecyanine of unsymmetrical structure [9]:



which has an absorption maximum in ethanol of 578 mμ. Condensation of the quaternary salt in pyridine with p-dimethylaminobenzaldehyde yielded the styryl derivative:



having an absorption maximum at 543 mμ.

EXPERIMENTAL

3-Methyl-4-p-tolylbenzo[f]quinolinium Iodide. N-p-Tolyl-2-naphthylamine (4 g), benzene (3 ml), and hydrochloric acid (sp. gr. 1.19; 1.8 ml) were introduced into a tube cooled in ice, and paraldehyde (2 ml) was added. The tube was sealed, and the contents were heated in a boiling water bath for 9-10 hours. The product of the condensation then had the appearance of a thick liquid, dark brown in color. The tube was opened, and the reaction mixture was treated several times with small portions of ether, which were stirred well with the reaction product, and then poured off. When the ether no longer became colored, the mass became very viscous. The crude quaternary chloride so obtained was dissolved in a small amount of alcohol and converted into the less soluble iodide by addition of 5 ml of a saturated solution of potassium iodide and heating for 5-6 minutes in a water bath. The mixture was cooled, and distilled water (50 ml) was added, when, in addition to the precipitated finely crystalline powder of quaternary salt, part of the product remained in the form of dark-brown viscous mass. The whole of the reaction product, in the form of a solution in aqueous alcohol, was heated at the boil for 30 minutes and then filtered hot. A yellow filtrate was obtained, and a small amount of semisolid resinous material remained on the filter. The filtrate was evaporated down on a water bath until an oily film formed on the surface; it was then set aside overnight to crystallize. The yellow crystalline precipitate was filtered off and washed with ether. The quaternary salt obtained melted at 185-186°. The semisolid mass that remained on the filter was dissolved in alcohol, a small amount of active charcoal was added to the solution, which was boiled for a few minutes and then filtered hot. On cooling, the solution yielded yellow crystals that melted at 187° and underwent the cyanine condensation in exactly the same way as the salt obtained from the first filtrate. The total yield of quaternary salt was 2.4 g (32%).

Found %: I 30.74
$C_{21}H_{18}NI$. Calculated %: I 30.82

Bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine Iodide. A mixture of 0.75 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.45 g of ethyl orthoformate, and 3 ml of pyridine was boiled in a small flask under reflux with continuous shaking for 25-30 minutes. As heating continued, the reaction mixture acquired a greenish color, which finally turned into an intense green. The solution was cooled, and the dye formed was precipitated with ether and dissolved in a small amount of alcohol. The alcoholic solution of dye was set aside overnight. On the next day the precipitated dye was filtered off and washed with small amounts of alcohol and ether. The dye, recrystallized from alcohol, formed dark-green crystals having a metallic reflex (0.27 g; 42.1%). It melted with decomposition at 225-227°. Its absorption maximum in ethanolic solution was 644 mμ.

Found %: I 17.76.
$C_{43}H_{33}N_2I$. Calculated %: I 18.01.

(4-p-Tolyl-3-benzo[f]quinoline)(1,3,3-trimethyl-2-pseudoindole)trimethinecyanine Iodide. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.44 g of 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)-pseudoindolium iodide, and 2 ml of pyridine was placed in a small flask fitted with reflux condenser and heated in a paraffin bath at 120-130° for 20-25 minutes. As heating proceeded the mass acquired a violet color, which became an intense bluish violet toward the end of the reaction. The mixture was cooled, and the dye was precipitated with ether and dissolved in 3 ml of alcohol; the solution was diluted with 5 ml of water and heated to the boil. On cooling, the aqueous-alcoholic mixture yielded dark-violet crystals of dye, which were filtered off and washed with ether. The dye was recrystallized from alcohol and was obtained as a crystalline powder having a greenish, metallic luster (0.21 g; 29.0%). It melted with decomposition at 243-245°. The absorption curve of the dye was determined in ethanolic solution on a spectrodensograph; the absorption maximum was 576 mμ.

Found %: I 21.10.
$C_{34}H_{31}N_2I$. Calculated %: I 21.35.

(4-p-Tolyl-3 benzo[f]quinoline)(3-ethyl-3-benzothiazole)trimethinecyanine Iodide. A mixture of 0.75 g of 3-methyl-4 p-tolylbenzo[f]quinolinium iodide, 0.55 g of 3-ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide, and 4 ml of pyridine was placed in a small flask and heated in a paraffin bath at 130-135° for 20-25 minutes with frequent shaking. As heating progressed, the reaction mixture acquired a stable bluish-violet color. After cooling, the dye was treated with ether, which was mixed with the dye in successive portions, which were poured off. The mass of dye obtained was dissolved in a small amount of alcohol by application of heat, and then reprecipitated with water; the dye was washed several times with water, until the water remained practically uncolored. The dye powder obtained was recrystallized from alcohol, yielding 0.29 g (35.4% calculated on the benzothiazole intermediate) of a dark-violet crystalline substance; m.p. 269-273° (dec.). Its absorption maximum was 596 mμ.

Found %: I 20.89
$C_{32}H_{27}N_2SI$. Calculated %: I 21.20

(4-p-Tolyl-3-benzo[f]quinoline)(1-methyl-4-quinoline)monomethinecyanine Iodide*. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.26 g of 1-methylquinolinium iodide, 4 ml of absolute alcohol, and 0.5 ml of a saturated solution of sodium ethoxide was heated in a boiling water bath for 15 minutes with continual shaking. The reaction mixture was cooled and treated several times with ether (until it no longer became colored). The dye formed was dissolved by heating it with 6 ml of alcohol, and the solution was set aside overnight. On the next day the dye that had crystallized out was filtered off and washed with ether and a small amount of alcohol. It formed a violet crystalline powder, and its alcoholic solution was raspberry-colored. Recrystallization from alcohol yielded 0.28 g (39.80%) of the monocyanine, m.p. 204-205° (dec.). The absorption maximum was 578 mμ.

Found %: I 22.33
$C_{33}H_{27}N_2I$. Calculated %: I 21.94

(4-p-Tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine Iodide. A mixture of 0.7 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.5 g of 3-ethyl-2-methylthiobenzothiazolium iodide, 8 ml of absolute alcohol, and 0.30 g of anhydrous sodium acetate was heated with continual shaking in a small flask fitted with reflux condenser for 15 minutes at 110-115° in a paraffin bath. The reaction mixture was cooled and treated with ether until a colored solution was no longer obtained. The residue was filtered off, and washed with ether and a small amount of alcohol. Recrystallization from alcohol yielded 0.53 g (54.37%) of a lemon-yellow crystalline powder, m.p. 221-224° (dec.). The alcoholic solution of the dye was light yellow. The absorption maximum of the dye in ethanolic solution was 495 mμ.

Found %: I 21.91
$C_{30}H_{25}N_2SI$. Calculated %: I 22.17

3-(p-Dimethylaminostyryl)-4-p-tolylbenzo[f]quinolinium Iodide. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.2 g of p-dimethylaminobenzaldehyde, and 3 ml of pyridine was placed in a small flask attached to a reflux condenser and heated in a paraffin bath at 120-130° for 30-40 minutes. As heating proceeded, the reaction mixture acquired a crimson color, which became more intense toward the end of the heating. The dye formed, after cooling, was treated with ether, which was added, well mixed with the dye, and poured off, the treatment being repeated until the ether was no longer colored. The residue of dye was dissolved by heating with a small amount of alcohol, and the solution was set aside until the next day, when the precipitated dye was filtered off and washed with ether and a small amount of alcohol. The dye so obtained was in the form of green needles having a metallic luster; it gave a crimson solution in alcohol. After recrystallization from alcohol, the dye (45% yield) melted at 289-291° (dec.). Its absorption maximum was at 543 mμ.

Found %: I 23.18
$C_{30}H_{27}N_2I$. Calculated %: I 23.40

SUMMARY

1. The quaternary salt 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, which has not been described previously, has been synthesized by the cyclization of N-p-tolyl-2-naphthylamine.

2. From this quaternary salt the following six dyes have been synthesized (wavelength at absorption maximum given in parentheses): bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine iodide (644 mμ); (4-p-tolyl-3-benzo[f]quinoline)(1,3,3-trimethyl-2-pseudoindole)trimethinecyanine iodide (576 mμ); (4-p-tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)trimethinecyanine iodide (596 mμ); (4-p-tolyl-3-benzo[f]quinoline)(1-methyl-4-quinoline)monomethinecyanine iodide (578 mμ); (4-p-tolyl-3 benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine iodide (495 mμ); and 3-(p-dimethylaminostyryl)-4-p-tolylbenzo[f]quinolinium iodide (543 mμ).

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*In the Russian text, here and in the Summary, this dye is named as a 2-quinoline (not 4-quinoline) derivative. The name has been altered to conform with the formula given above and with the indications given in the reference [9] cited. — Publisher.

3. It has been shown that the presence of p-tolyl in place of ethyl on the hetero nitrogen atom of the benzo[f]quinolinium residue results in a bathochromic shift in the absorption maximum of the dye.

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Institute of Organic Chemistry
of the USSR Academy of Sciences

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* See Consultants Bureau Translation, page 347.
** " " " " " 491.

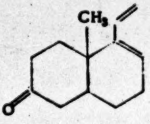
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXI. CONDENSATION OF 3,4,4a,5,8,8a-HEXAHYDRO-8a-METHYL-1-VINYLNAPHTHALENE WITH α,β-UNSATURATED CYCLIC KETONES.

SYNTHESIS OF STEROID KETONES DERIVED FROM HYDROGENATED CYCLOPENTA[a]PHENANTHRENE AND CHRYSENE*

I. N. Nazarov, L. I. Shmonina, and I. V. Torgov

In previous communications we have described the synthesis of the bicyclic dienes, I, II, III, and IV, which react comparatively readily not only with citraconic and maleic anhydrides, but also with the α,β-unsaturated cyclic ketones VI – X and the diketones XI and XII [1]: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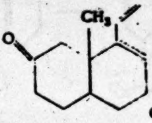
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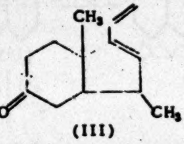
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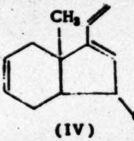
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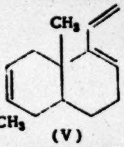
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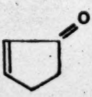
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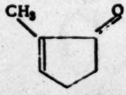
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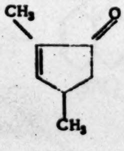
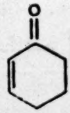

(VIII)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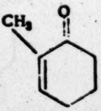
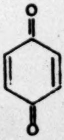
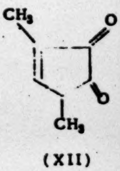

(X)


(XI)


(XII)

In this way we have succeeded in effecting for the first time the complete synthesis of numerous steroid ketones derived from hydrogenated cyclopenta[a]phenanthrene, chrysene, and benzofluorene, and having angular methyl groups.

The condensation of the bicyclic dienes I – IV with the α,β-unsaturated ketones VI – X generally resulted in the formation of a mixture of isomeric steroid ketones, differing, as we have shown [2], either in spatial configuration, or in the positions of the double bonds. The isomeric steroid ketones obtained by the condensation of the dienes I and II with 2-methyl-2-cyclopenten-1-one (VII) and 2,4-dimethyl-2-cyclopenten-1-one (VIII) have the so-called "inverted" structure, i.e., have the keto group of ring D in position 15, as, for example:

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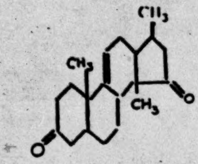
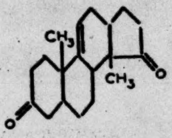
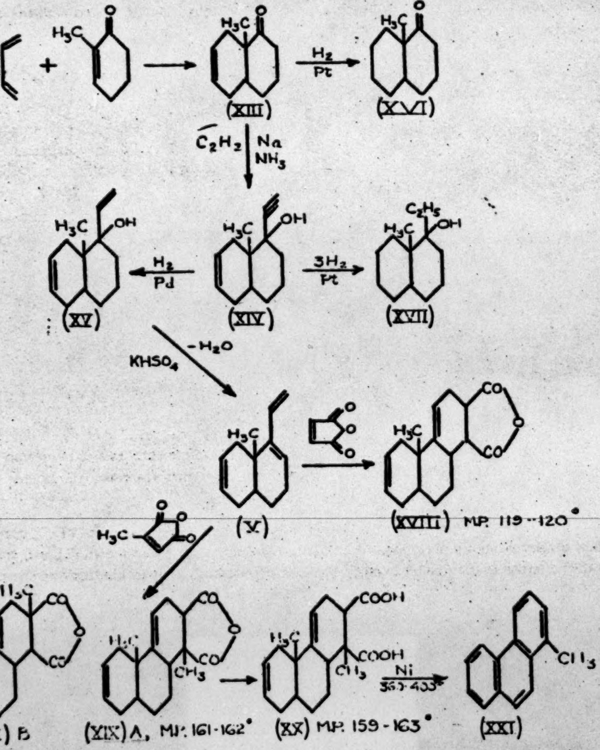

CH3
CH3
CH3
O
O



The condensation of the bicyclic dienes I – IV with other α,β-unsaturated cyclic ketones probably proceeds in a similar way, i.e., in these cases also isomers having an "inverted" D ring will predominate.

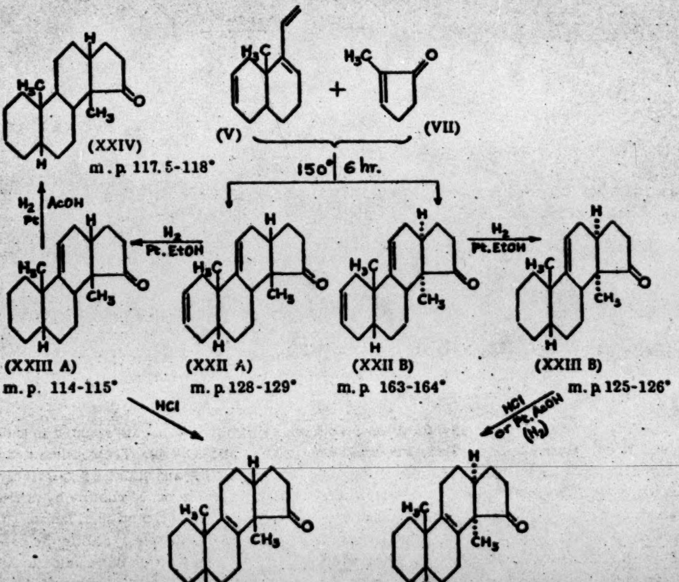
The present paper is devoted to an investigation of the condensation of the α,β-unsaturated cyclic ketones VII – XII with 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), which was prepared similarly to the dienes I – IV by the route shown in the following scheme:


H3C
O
(XIII)
H2
Pt
(XVI)
C2H2
Na
NH3
H3C
OH
H2
Pd
(XV)
(XIV)
3H2
Pt
C2H5
OH
(XVII)
KHSO4
- H2O
(V)
(XVIII) MP. 119--120°
H3C
(XIX) B
(XIX) A, MP. 161-162°
CH3
COOH
COOH
(XX) MP. 159 - 163°
Ni
360-400°
CH3
(XXI)

Heating of 1,3-butadiene with a four- or five-fold excess of 2-methyl-2-cyclohexen-1-one (X) in an autoclave at 245-250° for two hours yielded the previously described [1] cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone (XIII), which, on being hydrogenated in presence of platinum, absorbed one molecule of hydrogen and formed cis-octahydro-8a-methyl-1(2H)-naphthalenone (XVI). When XIII was condensed with sodium acetylide in liquid ammonia, an 80% yield of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV) was obtained; and selective hydrogenation of this over a palladium catalyst (1 molecule of hydrogen) yielded 1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-vinyl-1-naphthol (XV) quantitatively, whereas exhaustive hydrogenation (3 molecules of hydrogen) gave 1-ethyldecahydro-8a-methyl-1-naphthol (XVII). Dehydration of XV in a vacuum with the aid of finely ground, calcined potassium hydrogen sulfate at 130-140° gave a 70% yield of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), which readily underwent diene condensation with the α,β-unsaturated cyclic ketones VII – XII, and also with maleic and citraconic anhydrides. It condensed with maleic anhydride even at room temperature with evolution of heat, yielding the crystalline anhydride of 1,2,3,4b,5,8,8a,9,10,10a-decahydro-4b-methyl-1,2-phenanthrenedicarboxylic acid (XVIII).

The reaction between V and citraconic anhydride proceeds just as readily, yielding a mixture of crystalline isomers, probably having the structures XIX A and XIX B. From this mixture it was found possible to isolate the anhydride XIX A, which was hydrolyzed into the corresponding acid XX. The structure of this acid was proved by dehydrogenation in presence of Raney nickel in benzene at 360-400°, when 1-methylphenanthrene (XXI) was obtained. In this case it was not found possible to isolate the isomeric anhydride (XIX B), but its presence is confirmed by the analogous example of the condensation of citraconic anhydride with 1-vinyl-1-cyclohexene, which was performed recently in our laboratory: the two theoretically possible isomers were isolated.

Condensation of the hexahydromethylvinylnaphthalene V with 2-methyl-2-cyclopenten-1-one (VII) at 150° gave a 60% yield of a mixture of crystalline ketones, from which two isomers of 10,14-dimethyl-2,9-cardosteradien-15-one, XXII A and XXII B were isolated*. When these were hydrogenated in alcohol in presence of platinum,



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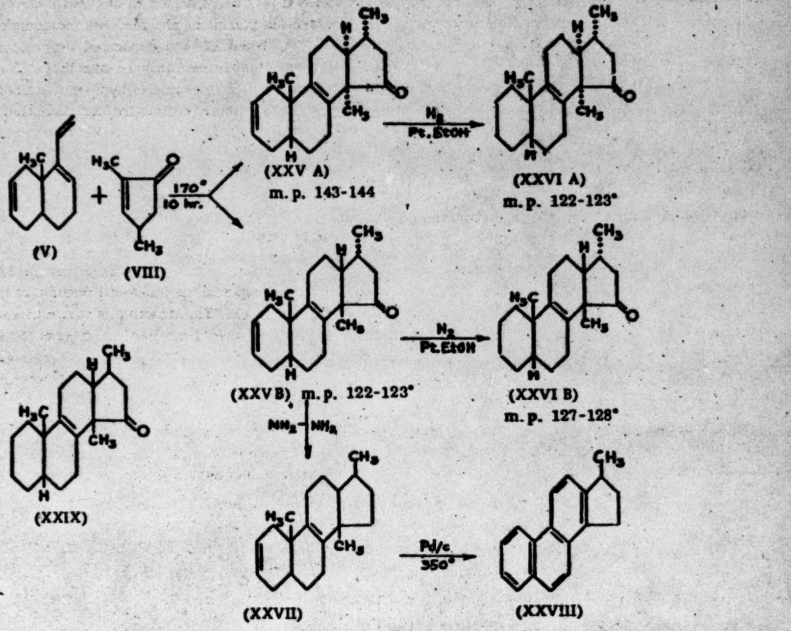
*The steroid compounds are named according to Nazarov's nomenclature for synthetic steroids; see Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 726 (Consultants Bureau Translation, p. 651). — Publisher.

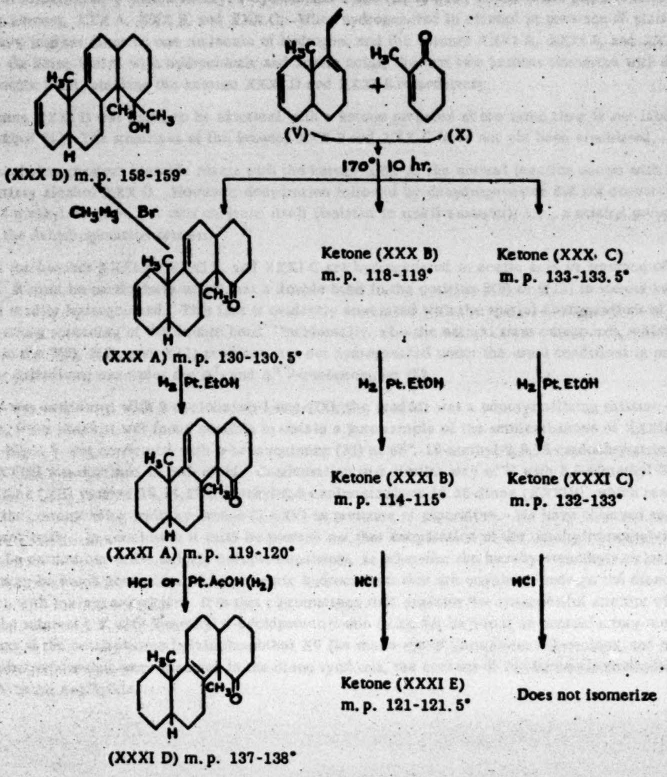


only one molecule of hydrogen was absorbed, i.e., the 9(11) double bond was not affected. The ketones (XXIII A and XXIII B) so obtained isomerized when boiled with hydrochloric and acetic acids with displacement of the double bond, yielding the ketones XXIII C and XXIII D, which were found to be identical with ketones obtained at the same time in our laboratory by another method; the structures of the latter have been proved [3]. This established also the structures of the ketones XXII A and XXII B (see the scheme on p. 957).

The ketone XXIII A, when hydrogenated over platinum in acetic acid, absorbed one molecule of hydrogen, yielding the fully saturated ketone XXIV. This is the first case in which the 9(11) double bond has been successfully hydrogenated in steroid ketones of this type. Under the same conditions, the ketones XXIII C and XXIII D were not hydrogenated at all, and the ketone XXIII B partially isomerized with displacement of the double bond, giving the ketone XXIII D.

Condensation of V with 2,4-dimethyl-2 cyclopenten-1-one (VIII) (at 170°) again resulted in the formation of two isomers, 10,14,17-trimethyl-2,9-cardosteradien-15-one (XXV A and XXV B). These, when hydrogenated over platinum, absorbed 1 molecule of hydrogen, giving the ketones XXVI A and XXVI B respectively. The ketone XXVI A was found to be identical with a ketone obtained at the same time in our laboratory by another method [2], and the structure of the latter was proved. The question of the structure of the original ketone (XXV A) was therefore solved. It is interesting to note that in this case, and, as we shall see below, also in the case of the ketone XXV B, the displacement of the double bond from the 9(11) to the 8(9) position occurs already in the course of the diene synthesis. We have found a similar case in the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-methyl-2 cyclohexen-1-one (X), and this is described in a previous communication [4].

As regards the ketone XXV B, we succeeded in converting it by a series of reactions into the so-called Diels hydrocarbon, 16,17-dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (XXVIII): Kizhner reduction of the ketone


H₃C
CH₃
CH₃
OH
H
(XXX D) m.p. 158-159°
H₃C
+
H₃C
O
(V)
(X)
170° 10 hr.
CH₃MgBr
H₃C
CH₃
O
H
(XXX A) m.p. 130-130.5°
Ketone (XXX B)
m.p. 118-119°
Ketone (XXX C)
m.p. 133-133.5°
H₂ Pt.EtOH
H₂ Pt.EtOH
H₂ Pt.EtOH
H₃C
CH₃
O
H
(XXXI A) m.p. 119-120°
Ketone (XXXI B)
m.p. 114-115°
Ketone (XXXI C)
m.p. 132-133°
HCl or Pt.AcOH(H₂)
HCl
HCl
H₃C
CH₃
O
H
(XXXI D) m.p. 137-138°
Ketone (XXXI E)
m.p. 121-121.5°
Does not isomerize

XXV B gave the hydrocarbon XXVII, which was dehydrogenated at 350° over palladized charcoal; the Diels hydrocarbon (XXVIII) was then isolated from the reaction mixture by chromatography. The melting points of the hydrocarbon and of its trinitrobenzene addition compound corresponded to the values given in the literature, and the respective mixed melting point tests gave no depression. The ketone XXV B, therefore, also has the "inverted" structure (see scheme on p. 958).

It must be pointed out that proof of the structures of the ketones XXVI by a second method that we have applied previously, namely oxidation of the D ring with an alkaline solution of iodide followed by dehydrogenation of the dicarboxylic acid formed into ethylmethylphenanthrene, was not found possible: in the oxidation iodine-containing products were obtained that were unsuitable for the subsequent dehydrogenation.

When heated with hydrochloric and acetic acids, neither of the ketones XXVI A and XXVI B changed. In a similar way, they were not hydrogenated in presence of platinum in acetic acid. These facts lead us to conclude that in these ketones, and therefore also in the ketones XXV A and XXV B, the double bond is not, as usual in the 9(11) position, but in the 8(9) position. Otherwise these ketones would have undergone isomerization. The displacement of the double bond evidently occurred in the course of the diene synthesis. The difference between the ketones XXV B and XXVI B and their isomers XXV A and XXVI A probably lies in the different spatial arrangement of the ($C_{13}-C_{14}$) substituents. The difference between the ketone XXVI B and the ketone XXIX previously obtained in our laboratory [2] is probably to be explained by a difference in the spatial configuration of the methyl at C_{13}.

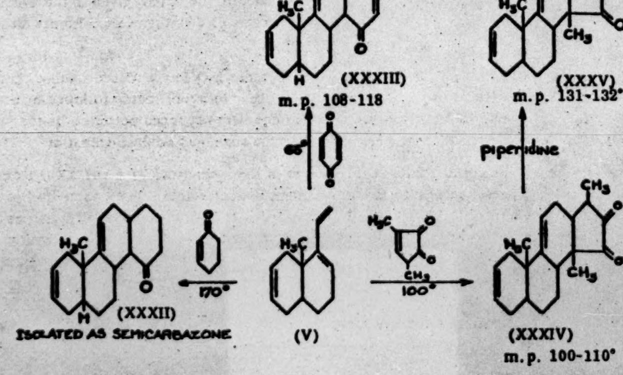
In the condensation of V with 2-methyl-2-cyclohexen-1-one (X) at 170°, it was found possible to isolate three isomeric ketones, XXX A, XXX B, and XXX C. When hydrogenated in alcohol in presence of platinum, each of the three isomers takes up one molecule of hydrogen, and the ketones XXXI A, XXXI B, and XXXI C, are obtained. On being boiled with hydrochloric and acetic acids, the first two ketones isomerize with displacement of the double bond, yielding the ketones XXXI D and XXXI E respectively.

The ketone XXXI D was found to be identical with a ketone prepared at the same time in our laboratory by another method [4]. The structures of the ketones XXX B and XXX C have not yet been elucidated.

When methylmagnesium bromide reacts with the ketone XXX A, the normal reaction occurs with formation of the tertiary alcohol XXX D. However, dehydration followed by dehydrogenation did not convert it into the expected 4-methylchrysene, but into chrysene itself (isolated in small amounts); i.e., a methyl group was eliminated in the dehydrogenation process.

None of the ketones XXXI A, XXXI B, and XXXI C are hydrogenated in acetic acid in presence of a platinum catalyst. It must be particularly noted that a double bond in the position 8(9) or 9(11) in steroid ketones is in general not readily hydrogenated. This fact is evidently associated with the spatial configurations of the ketones and the strong screening of the double bond. Incidentally, also the natural trans compounds, which have double bonds in the 7(8), 8(9), and 9(11) positions, are not hydrogenated under the usual conditions in presence of platinum or palladium; examples are Δ^7- and $\Delta^{8(9)}$-cholestenones [5].

When V was condensed with 2-cyclohexen-1-one (IX), the product was a noncrystallizing mixture of isomeric ketones, from which it was found possible to obtain a pure sample of the semicarbazone of XXXII (m.p. 237-237.5°). When V was condensed with p-benzoquinone (XI) at 65°, 10-methyl-2,9,16-cardochrysatriene-15,17a-dione (XXXIII) was obtained in 30% yield. Condensation in a similar way of V with 3,5-dimethyl-3-cyclopentene-1,2-dione (XII) yielded 10,14,17-trimethyl-2,9-cardosteradiene-15,16-dione (XXXIV), which readily isomerized into the corresponding hydroxy ketone (XXXV) in presence of piperidine. We have observed such isomerizations previously. In conclusion it must be pointed out that dehydration of the octahydromethylvinylnaphthol XV must be carried out under strictly defined conditions, as otherwise the hexahydromethylvinylnaphthalene obtained (V) may be much contaminated by isomeric hydrocarbons that are unable to undergo the diene condensation even with maleic anhydride. It is this circumstance that explains the unsuccessful attempt of Butz [7] to condense the substance V with 2-methyl-2-cyclopenten-1-one (VII), for he chose an unsatisfactory method for the dehydration of the octahydromethylvinylnaphthol XV (he made use of phosphorus tribromide), and obtained a mixture of hydrocarbons that were inactive in the diene synthesis, the content of the hexahydromethylvinylnaphthalene V being negligible.



EXPERIMENTAL

2-Methyl-2-cyclohexen-1-one (X) [b.p. 66-67° (15 mm); n_D^{20} 1.4860], 2-cyclohexen-1-one (IX) [b.p. 83° (40 mm); n_D^{20} 1.4845], and 2-methyl-2-cyclopenten-1-one (VII) [b.p. 57° (15 mm); n_D^{20} 1.4778] were prepared by a method developed in our laboratory [8]. 2,4-Dimethyl-2-cyclopenten-1-one (VIII) [b.p. 164-165°; n_D^{20} 1.4672] was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one [8]. 3,5-Dimethyl-3-cyclopentene-1,2-dione (XII) (m.p. 65-66°) was prepared by the oxidation of 2,4-dimethyl-2-cyclopenten-1-one with selenium dioxide [9]. Citraconic anhydride [b.p. 81° (2 mm); n_D^{20} 1.4710] was prepared by Shriner's method [16].

Condensation of 2-Methyl-2-cyclohexen-1-one (X) with 1,3-Butadiene. A mixture of 582 g of 2-methyl-2-cyclohexen-1-one (X), 75 g of 1,3-butadiene, and 2.5 g of diethylaniline was heated for two hours at 245-250° in a rotating stainless-steel autoclave. Vacuum distillation of the reaction mixture yielded 543 g of unchanged methylcyclohexenone and 26.5 g (45% on the ketone that had reacted) of a product of b.p. 93-95° (4 mm). In this way altogether 338 g of cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone (XIII) was obtained as a fairly mobile liquid having a characteristic odor; b.p. 82-84° (2 mm); n_D^{20} 1.5050.

	Found %:	C 80.8; H 10.2
$C_{11}H_{16}O$.	Calculated %:	C 80.5; H 9.8

The semicarbazone melted at 225° with some decomposition (in a sealed capillary).

	Found %:	N 19.0; 18.95
$C_{12}H_{19}ON_3$.	Calculated %:	N 19.0

Butz [10] gives the following constants for cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone: b.p. 67° at 0.5 mm; n_D^{20} 1.5042; and for the semicarbazone, m.p. 224.8-225°.

Hydrogenation of cis-3,4,4a,5,8,8a-Hexahydro-8a-methyl-1(2H)-naphthalenone (XIII). Some of the substance XIII (1.6 g) was hydrogenated in 5 ml of alcohol in presence of a platinum catalyst. Hydrogenation was continued for 40 minutes, and 245 ml of hydrogen (18°, 760 mm) was absorbed (theory requires 238 ml). Distillation yielded 1.3 g of cis-octahydro-8a-methyl-1(2H)-naphthalenone (XVI), b.p. 84-86° (3 mm); n_D^{20} 1.4950.

	Found %:	C 79.7; 79.7; H 10.8; 10.9
$C_{11}H_{18}O$.	Calculated %:	C 79.5; H 10.8

The dinitrophenylhydrazone recrystallized from methanol melted at 159-160°. The literature [11] gives for XVI itself b.p. 72-73° (0.8 mm); n_D^{20} 1.4895; and for its dinitrophenylhydrazone, m.p. 162.4-165.2°.

Condensation of cis-3,4,4a,5,8,8a-Hexahydro-8a-methyl-1(2H)-naphthalenone (XIII) with Acetylene. a) A solution of XIII (115 g) in 200 ml of absolute ether was placed in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene. The flask was cooled with a mixture of solid carbon dioxide and methanol (−70°), and the solution was saturated with acetylene for one hour (about 40 liters). Then, with continuous stirring and passage of acetylene, a suspension of potassium 1,1-dimethylpentyloxide (56 g of potassium was dissolved by heat in 350 ml of 2-methyl-2-hexanol) in 1 liter of absolute ether was added to the solution of ketone, and acetylene was passed (3-5 liters per hour) for a further 13 hours at −70°. The mixture was then set aside overnight, and on the next day acetylene was passed (3-5 liters per hour) for eight hours at −5°. The reaction mixture was decomposed with 150 ml of water, the ether layer was separated, and the aqueous layer was extracted with ether. The united ether extracts were neutralized with acetic acid and dried with sodium sulfate; the ether was driven off, and the residue was vacuum-fractionated, yielding 23 g of unchanged XIII and 80 g of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV), a thick colorless liquid of characteristic odor, which gave a voluminous precipitate with an ammonical solution of silver oxide. The yield was 80% on the ketone that reacted; b.p. 98-99° (1.5 mm); n_D^{20} 1.5240.

	Found %:	C 82.3, 82.3; H 9.7, 9.5
$C_{13}H_{18}O$.	Calculated %:	C 82.1; H 9.5

Butz and coworkers [11] give the following constants for the tertiary alcohol XIV: b.p. 76-78° (0.3 mm); n_D^{20} 1.5275.

b) Liquid ammonia (1000 ml) was placed in the above-described flask, and with stirring at −70° sodium (38 g) was added in small pieces. The mixture was stirred for 20 minutes, and acetylene was then passed at 25-30 liters per hour for 3 hours 30 minutes. The rate of passage was then reduced to 15 liters per hour, and over a period of two hours a solution of 133 g of XIII in 150 ml of absolute ether was added. Passage of acetylene was continued for a further 90 minutes at the same rate, and the mixture was then set aside at −70° overnight. On the next day stirring and passage of acetylene (15 liters per hour) were continued for two hours at −60°. The cooling bath was then removed, and when the temperature of the mixture rose to −35° the reaction mixture was decomposed by cautious addition of 150 g of ammonium chloride. When the ammonia had evaporated away and the temperature had risen to 0°, 200 ml of ether and 300 ml of water were added. The ether layer was separated, the aqueous layer was extracted with ether, and the united extracts were dried with sodium sulfate. The solvent was driven off, and the residue was vacuum-fractionated, yielding 125 g (86%) of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV), b.p. 97-99° (2 mm); n_D^{20} 1.5245.

Exhaustive Hydrogenation of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV). Some of the acetylenic alcohol XIV (1.5 g) was hydrogenated in 8 ml of alcohol in presence of a platinum catalyst. The amount of hydrogen absorbed was 587 ml (21°, 760 mm) (theory required 572 ml). The alcohol was driven off, and vacuum distillation of the residue yielded 1.2 g of 1-ethyldecahydro-8a-methyl-1-naphthol (XVII) as a thick colorless liquid of characteristic odor; b.p. 83-84° (0.05 mm); n_D^{20} 1.5060.

Found %: C 79.3, 79.3; H 12.3, 12.3
$C_{13}H_{24}O$. Calculated %: C 79.6; H 12.25

After standing for three months, the liquid partially crystallized. The crystals were washed with ether and then melted at 62-63°.

Found %: C 79.8, 79.65; H 12.3, 12.0
$C_{13}H_{24}O$. Calculated %: C 79.6; H 12.25

The ethyldecahydromethylnaphthol XVII was probably obtained in the form of two stereoisomers differing in the configuration at C_1. The original acetylenic alcohol XIV, therefore, must have been a mixture of stereoisomers differing in the configuration at C_1.

Preparation of 1,2,3,4,4a,5,8,8a-Octahydro-8a-methyl-1-vinyl-1-naphthol (XV). The acetylenic alcohol XIV (80 g) was hydrogenated in 100 ml of alcohol in presence of palladium on a calcium carbonate carrier. Hydrogenation was continued for 3 hours 30 minutes, and was interrupted when 9700 ml of hydrogen (21°, 760 mm) had been absorbed, since a test for a triple bond was negative (theory requires the absorption of 10,100 ml of hydrogen). After filtration and removal of alcohol, vacuum-distillation yielded 77 g of 1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-vinyl-1-naphthol (XV) as a thick colorless liquid having a feeble odor; b.p. 91-93° (2 mm); n_D^{20} 1.5215.

Found %: C 81.2; H 10.4
$C_{13}H_{20}O$. Calculated %: C 81.25; H 10.4

Butz and coworkers [12] give the following constants for the tertiary alcohol XV: b.p. 76-80° (0.3 mm); n_D^{20} 1.5226.

Dehydration of 1,2,3,4,4a,5,8,8a-Octahydro-8a-methyl-1-vinyl-1-naphthol (XV). A mixture of 4.5 g of the ethylenic alcohol XV and 2.5 g of finely ground potassium hydrogen sulfate was heated at 130-140° for 30 minutes at reduced pressure (100-110 mm). The product was then distilled from the reaction mixture at 3 mm, dried with calcium chloride, and again distilled, yielding 3 g (75%) of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), a slightly yellowish mobile liquid of characteristic odor; b.p. 74-74.5° (1 mm); n_D^{20} 1.5250.

Found %: C 89.4, 89.4; H 10.7, 10.5
$C_{13}H_{18}$. Calculated %: C 89.65; H 10.35

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with Maleic Anhydride. A mixture was made of 0.3 g of the hexahydromethylvinylnaphthalene and 0.17 g of maleic anhydride; there was noticeable evolution of heat. In order to complete the reaction, the mixture, diluted with 1 ml of absolute benzene, was heated in a sealed tube in a boiling water bath for three hours. When the benzene had evaporated away, the mass crystallized out. Two crystallizations from hexane gave the pure anhydride of 1,2,3,4b,5,8,8a,-9,10a-decahydro-4b-methyl-1,2 phenanthrenedicarboxylic acid (XVIII), m.p. 119-120° (in a sealed capillary).

Found %: C 75.15; H 7.4
$C_{17}H_{20}O_3$. Calculated %: C 75.00; H 7.4

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with Citraconic Anhydride. a) A mixture of 1.6 g of V and 1.2 g of citraconic anhydride in 2 ml of absolute benzene was left in a sealed tube at room temperature for one day and was then heated at 100° for seven hours. After removal of benzene the residue crystallized out, yielding 0.8 g (30%) of a mixture of the anhydrides XIX A and XIX B, m.p. 133-145°, in which the anhydride XIX A predominated. Crystallization from hexane gave crystals of m.p. 135-150° (in a sealed capillary).

	Found %: C 75.9; H 7.9
$C_{18}H_{22}O_3$.	Calculated %: C 75.5; H 7.7

Further recrystallization from hexane yielded a small amount of pure crystals, m.p. 161-162° (in a sealed capillary).

	Found %: C 75.6, 75.8; H 7.7, 7.8
$C_{18}H_{22}O_3$.	Calculated %: C 75.5; H 7.7

b) A mixture of 6.5 g of V, 4.2 g of citraconic anhydride, and 3 ml of absolute benzene was left for two days in a sealed tube at room temperature. The mixture partially crystallized out, and 3.5 g of crystals, m.p. 120-135°, was separated. The liquid portion remaining after separation of the crystals was heated for six hours in a sealed tube in a boiling water bath. The liquid remaining after removal of benzene did not crystallize; citraconic anhydride (2 g) was added to it, and heating was continued for a further six hours at 125°. After removal of the excess of citraconic anhydride by distillation and treatment of the residue with absolute methanol, a further 0.3 g of crystals, m.p. 105-135°, was obtained (total yield 36%). Fractional crystallization from a mixture of hexane and benzene did not result in the isolation of a pure product. Mixtures of crystals of the following melting points were separated: 159-163°; 153-162°; 134-139° (in sealed capillaries).

Hydrolysis of the Anhydrides XIX A and XIX B. The crystalline mixture of anhydrides (0.3 g; m.p. 134-139°) was heated with 12 ml of 50% acetic acid for six hours at 90° and three hours at 103-105°. The crystals that came down on cooling were recrystallized from 50% acetic acid, and they melted at 159-163° (in a sealed capillary).

	Found %: C 70.8, 70.95; H 8.1, 8.1
$C_{18}H_{24}O_4$.	Calculated %: C 71.0; H 7.9

The crystalline mixtures of anhydrides of m.p. 159-163° and 153-162° were also hydrolyzed under the same conditions. In both cases crystals of an acid of m.p. 159-163° were isolated, and these gave no melting-point depression in admixture with the analyzed sample.

The fact that different mixtures of the anhydrides give the same substance when hydrolyzed evidently indicates that the corresponding acids have close melting points and identical solubility and are therefore not separated, but give a constant mixture of m.p. 159-163°.

Dehydrogenation and Decarboxylation of 1,2,3,4b,5,8,8a,9,10,10a-Decahydro-1,4a-dimethyl-1,2-phenanthrene dicarboxylic Acid (XX). The above-described acid (m.p. 159-163°) (0.7 g), 25 ml of dry benzene, and 3 g of nickel catalyst were heated in a 200-ml autoclave for 17 hours at 360-380°, 3 hours at 380-400°, and 3 hours 30 minutes at 400-410°. The residue after evaporation of the benzene consisted of 0.5 g of a dark-colored viscous mass, from which, after 10-12 hours, 100 mg of crude 1-methylphenanthrene crystals separated (XXI). Three crystallizations from methanol yielded 60 mg of crystals of m.p. 120-122° (in a sealed capillary).

	Found %: C 93.55, 93.8; H 6.40, 6.5
$C_{15}H_{12}$.	Calculated %: C 93.75; H 6.25

The picrate melted at 132° (from alcohol).

For 1-methylphenanthrene the literature gives m.p. 118° [13], 120-121° [14], and for the picrate: m.p. 135-136° [13], 139° [14].

2-Methylphenanthrene melts at 56-57°, and its picrate at 118-119° [15].

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Methyl-2-cyclopenten-1-one (VII). A mixture of 10 g of the hexahydromethylvinylnaphthalene V and 20 g of the methylcyclopentenone VII was heated in a sealed tube in an atmosphere of carbon dioxide for six hours at 150°. The excess (17 g) of the methylcyclopentenone was distilled off under reduced pressure (15 mm), and the residue then crystallized out, yielding 8.6 g (55%) of a mixture of the isomeric steroid ketones XXII A and XXII B, m.p. 90-123°. By this method altogether 24 g of the mixture of isomers was obtained and then fractionally crystallized, yielding 6 g of ketone XXII A, m.p. 128-129° and 4 g of ketone XXII B, m.p. 163-164°.

Analysis of Ketone XXII A

	Found %: C 84.3, 84.3; H 9.7, 9.8
$C_{19}H_{26}O$.	Calculated %: C 84.4; H 9.6

Analysis of Ketone XXII B

Found %: C 84.1, 84.2; H 9.6, 9.7

$C_{19}H_{26}O$. Calculated %: C 84.4; H 9.6

Hydrogenation of Ketones XXII A and XXII B. The ketone XXII A of m.p. 128-129° (1.4 g) was hydrogenated in 40 ml of methanol in presence of an Adams platinum catalyst. Hydrogenation was complete in 90 minutes, the amount of hydrogen absorbed being 146 ml (26°, 755 mm) (128 ml theoretically required). The usual treatment and crystallization from methanol yielded 1.2 g of the ketone XXIII A, m.p. 114-115°.

Found %: C 84.0; H 10.4

$C_{19}H_{28}O$. Calculated %: C 83.8; H 10.3

In the same way, hydrogenation of 0.8 g of ketone XXII B of m.p. 163-164° yielded 0.7 g of the ketone XXIII B, m.p. 125-126°.

Found %: C 83.8; H 10.4

$C_{19}H_{28}O$. Calculated %: C 83.8; H 10.3

Hydrogenation of Ketone XXIII A. The ketone XXIII A of m.p. 114-115° (200 mg) was hydrogenated in 5 ml of acetic acid in presence of an Adams platinum catalyst (50 mg). The usual treatment and crystallization from petroleum ether yielded 55 mg of the ketone XXIV, m.p. 117.5-118°.

Found %: C 83.1, 83.2; H 11.3, 11.45

$C_{19}H_{30}O$. Calculated %: C 83.2; H 10.95

The melting point of the ketone obtained (XXIV) was depressed (to 106-110°) when mixed with the original ketone.

Isomerization of the Ketone XXIII A. A mixture of 0.7 g of ketone XXIII A, m.p. 114-115°, 13 ml of acetic acid, 11 ml of concentrated hydrochloric acid, and 15 ml of toluene was boiled under reflux for ten hours. The toluene layer was separated, neutralized by agitation with 5% caustic soda, filtered, and distilled to remove solvent. The residue was crystallized from petroleum ether, yielding 0.5 g of the ketone XXIII C, m.p. 52-54°. In admixture with the ketone obtained at the same time in our laboratory by another method [3] it showed no melting point depression. The ketone XXIII C did not undergo hydrogenation in acetic acid in presence of a platinum catalyst.

Isomerization of the Ketone XXIII B. a) The isomerization was effected in presence of hydrochloric acid, as described above; from 100 mg of ketone XXIII B, m.p. 125-126°, 30 mg of ketone XXIII D, m.p. 95-96° was obtained. In admixture with the ketone of m.p. 92-93° obtained at the same time in our laboratory by another method [3] it showed no melting point depression.

b) A mixture of 200 mg of the ketone XXIII B, m.p. 125-126°, and 5 ml of acetic acid was shaken in an atmosphere of hydrogen in presence of 50 mg of Adams platinum oxide for two hours. The usual treatment and crystallization from petroleum ether yielded 20 mg of the original ketone (m.p. 119-121°; satisfactory mixed m.p.) and 100 mg of ketone XXIII D, m.p. 92-93° (no depression in admixture with above-described sample of the ketone).

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2,4-Dimethyl-2-cyclopenten-1-one (VIII). A mixture 6 g of the triene V and 24 g of 2,4-dimethyl-2-cyclopenten-1-one (VIII) (b.p. 164-165°; n_D^{28} 1.4672) was heated for ten hours at 170° in a glass tube in an atmosphere of carbon dioxide. Excess (18 g) of the ketone was distilled off under reduced pressure (15 mm), and a mixture of petroleum ether and benzene (10 ml, 10:1) was added to the residue, when the mass partially crystallized out. Fractional crystallization from methanol yielded 1.3 g of ketone XXV A, m.p. 143-144°, and 1.6 g of ketone XXV B, m.p. 122-123°

Analysis of the Ketone XXV A

Found %: C 84.4, 84.6; H 9.8, 9.95

$C_{20}H_{28}O$. Calculated %: C 84.5; H 9.9

Analysis of the Ketone XXV B

Found %: C 84.4, 84.5; H 9.8, 9.9

$C_{20}H_{28}O$. Calculated %: C 84.5; H 9.9

Attempts to form derivatives by reaction at the carbonyl group were not successful.

Hydrogenation of the Ketone XXV A. The ketone XXV A of m.p. 143-144° (150 mg) was hydrogenated in 10 ml of alcohol in presence of an Adams platinum catalyst (10 mg). Hydrogenation was complete in five minutes, when 14.1 ml (22°, 760 mm) of hydrogen had been absorbed (theory requires 14.7 ml, hydrogen consumed in the reduction of the platinum oxide being taken into account). The usual treatment and crystallization from petroleum ether yielded 70 mg of the ketone XXVI A, m.p. 122-123°.

Found %: C 83.6; H 10.5
$C_{20}H_{30}O$. Calculated %: C 83.9; H 10.5

In admixture with the ketone prepared in our laboratory by another method [2] there was no depression in melting point.

An attempt to bring about the isomerization of the ketone XXVI A in boiling hydrochloric and acetic acids gave a negative result, the ketone being recovered unchanged. Moreover, the ketone was not hydrogenated when treated in presence of a platinum catalyst in acetic acid.

Hydrogenation of the Ketone XXV B. The ketone XXV B, m.p. 122-123° (150 mg), was hydrogenated in alcohol in the manner described above, the product being 60 mg of the ketone XXVI B, m.p. 127-128°.

Found %: C 83.8, 83.9; H 10.5, 10.7
$C_{20}H_{30}O$. Calculated %: C 83.9; H 10.5

In admixture with the original ketone it melted at 104-117°. The ketone XXVI B could not be hydrogenated in acetic acid in presence of platinum and did not undergo isomerization in boiling hydrochloric and acetic acids.

Attempt to Oxidize the Ketone XXV B with Iodine and Alkali. Solutions of 2.65 g of iodine in 25 ml of methanol and of 5 g of caustic potash in a mixture of 10 ml of water and 15 ml of methanol were added with stirring to a solution of 1 g of the ketone XXV B, m.p. 122-123°, in 25 ml of methanol. The addition was carried out at 20° over a period of 50 minutes, care being taken that there was always excess of iodine. When half of the solutions had been added, a precipitate began to form, and this gradually increased in amount. The mixture was stirred for five hours, and the precipitate was then filtered off and washed with methanol (350 mg of fine crystals). Crystallization from methanol yielded 220 mg of a diiodo compound, m.p. 128-129° (softening, however, at 117°).

Found %: C 44.7, 44.6; H 5.5, 5.3; I 47.2, 47.5
$C_{20}H_{30}OI_2$. Calculated %: C 44.4; H 5.6; I 47.0

Kizhner Reduction of the Ketone XXV B. The ketone XXV B of m.p. 122-123° (1.7 g) was mixed with 5 ml of diethylene glycol, 7 ml of dioxane, and 1.2 ml of hydrazine hydrate, and heated for five minutes in a water bath. The mixture was transferred to a Favorsky flask having ground joints, and a solution of 1.4 g of sodium in 28 ml of diethylene glycol was added. The turbid mixture was heated in a feeble current of nitrogen at 205-210° for 15 hours, when the dioxane and a small amount of water were driven off.

The reaction mixture was diluted with twice its volume of water and extracted with ether; the ether extracts were washed twice with 10% hydrochloric acid and with water. The ether was driven off, and the residue was vacuum-distilled, yielding 1.3 g (81%) of the hydrocarbon XXVII as a thick colorless, almost odorless liquid, b.p. 145-147° (2 mm) and n_D^{20} 1.5330.

Found %: C 88.2; H 11.1
$C_{20}H_{30}$. Calculated %: C 88.9; H 11.1

Dehydrogenation of the Hydrocarbon XXVII. A mixture of 1.1 g of the hydrocarbon XXVII, 1.2 g of palladized charcoal (10% Pd), and 18 ml of benzene was heated in a rotating autoclave in an atmosphere of nitrogen (initial pressure, 30 atm) at 350° for six hours. After filtration and removal of benzene, the residue (0.9 g) was dissolved in 7 ml of petroleum ether and set aside at −70° for two days. Crystals (26 mg), m.p. about 90°, separated. The mother liquor was chromatographed through 10 g of aluminum oxide, and a further 30 mg of crystalline product was isolated as a result. The crops of crystals were united and crystallized twice from petroleum ether, yielding 20 mg of hydrocarbon XXVIII, m.p. 119-121°. In admixture with Diels' hydrocarbon, prepared previously by another method [2], it showed no depression in melting point.

Its compound with trinitrobenzene melted at 146-147°, and again it gave no depression in admixture with an authentic sample.

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Methyl-2-cyclohexen-1-one (X). A mixture of 10 g of V with 90 g of 2-methyl-2-cyclohexen-1-one (X) was heated for ten hours at 170°

in a glass tube in an atmosphere of carbon dioxide. The excess (84 g) of ketone was distilled off at 15 mm, and unchanged hydrocarbon (3 g) was distilled off at 1 mm. The residual viscous liquid (10 g) was mixed with 10 ml of alcohol, and crystallization quickly set in. Altogether (including material obtained from the mother liquors) 4.7 g of a crystalline mixture of steroid ketones was obtained (43% yield, based on the triene V that had reacted). Fractional crystallization from methanol yielded:

1. Ketone XXX A, m.p. 130-130.5°, 2.0 g.

Found %: C 84.3, 84.3; H 9.9, 9.9
$C_{20}H_{28}O$. Calculated %: C 84.5; H 9.9

After being washed with benzene, the semicarbazone melted at 245-247° (in a sealed capillary).

Found %: N 12.5, 12.6
$C_{21}H_{31}ON_3$. Calculated %: N 12.3

2. Ketone XXX B, m.p. 118-119°, 0.6 g.

Found %: C 84.5, 84.4; H 9.6, 10.0
$C_{20}H_{28}O$. Calculated %: C 84.5; H 9.9

3. Ketone XXX C, m.p. 133-133.5°, 0.4 g.

Found %: C 84.4, 84.6; H 9.9; 9.9
$C_{20}H_{28}O$. Calculated %: C 84.5; H 9.9

A mixture of ketone XXX C with ketone XXX A melted at 102-107°.

Hydrogenation of the Ketones XXX A, XXX B, and XXX C. The ketone XXX A of m.p. 130-130.5° (100 mg) was hydrogenated in 10 ml of alcohol in presence of an Adams platinum catalyst (the amount of hydrogen used was not measured). The usual treatment, followed by crystallizations from alcohol and from petroleum ether, yielded 40 mg of the ketone XXXI A, m.p. 119-120°.

Found %: C 84.0, 83.7; H 10.4, 10.55
$C_{20}H_{30}O$. Calculated %: C 83.9; H 10.5

In a similar way, 150 mg of ketone XXX B, m.p. 118-119°, yielded 50 mg of the ketone XXXI B, m.p. 114-115° (after two crystallizations from methanol).

Found %: C 84.0, 83.9; H 10.7, 10.7
$C_{20}H_{30}O$. Calculated %: C 83.9; H 10.5

In admixture with the original ketone (XXX B) it melted at 101-107°.

From 150 mg of the ketone XXX C, m.p. 133-133.5°, 40 mg of the ketone XXXI C, m.p. 132-133° (from methanol), was obtained.

Found %: C 83.7, 83.8; H 10.6, 10.7
$C_{20}H_{30}O$. Calculated %: C 83.9; H 10.5

In admixture with the original ketone (XXX C), a considerable depression in melting point was obtained.

Isomerization of the Ketone XXXI A. a) A mixture of 200 mg of the ketone XXXI A, m.p. 119-120°, 5 ml of acetic acid, 5 ml of hydrochloric acid, and 7 ml of toluene was boiled under reflux for seven hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was driven off under reduced pressure, and the residue was crystallized from petroleum ether, yielding 150 mg of the ketone XXXI D, m.p. 137-138°. This ketone showed no depression when mixed with the ketone obtained at the same time in our laboratory by another method [4] (see the ketone VII in Communication 155).

b) The ketone XXXI A of m.p. 119-120° (100 mg) was shaken in 5 ml of acetic acid in an atmosphere of hydrogen in presence of an Adams platinum catalyst for two hours. The usual treatment and crystallization from petroleum ether yielded 80 mg of the ketone XXXI D, m.p. 137-138°; in admixture with the ketone prepared as above (a), it showed no depression in melting point.

Isomerization of the Ketone XXXI B. This was carried out by the action of hydrochloric acid, as described above, 100 mg of the ketone XXXI B, m.p. 114-115°, yielding 60 mg of the ketone XXXI C, m.p. 121-121.5° (from alcohol). The ketone XXXI C was not affected by the action of hydrochloric acid.

Action of Methylmagnesium Bromide on the Ketone XXX A. A solution of 1.2 g of the ketone XXX A, m.p. 130°, in a mixture of 25 ml of ether and 10 ml of benzene was added with stirring to a Grignard reagent prepared from 0.5 g of magnesium, 3.1 g of methyl bromide, and 25 ml of absolute ether. The ether was driven off and replaced by 20 ml of benzene, and the mixture was heated at 80° for two hours. The mixture, on cooling, was decomposed with ice followed by hydrochloric acid. The benzene layer was dried, and the solvent was distilled off. The residue crystallized out and was recrystallized from methanol, yielding 0.9 g of the tetracyclic alcohol XXX D, m.p. 158-159°.

Found %: C 83.9, 84.1; H 10.9, 10.8
$C_{21}H_{32}O$. Calculated %: C 84.0; H 10.7

The tertiary alcohol obtained (XXX D) was dehydrated with potassium hydrogen sulfate in xylene at 150°. The product, without purification, was dehydrogenated in presence of palladized charcoal at 340-350°. Chromatography of the product yielded 8 mg of chrysene, m.p. 243-245°. Its compound with trinitrobenzene melted at 186.5-187°.

The following data regarding chrysene, 1-methylchrysene and 4-methylchrysene are given in the literature:

Substance	Reference	M.p. (°C)	M. p. (°C) of trinitrobenzene compound
Chrysene	[17]	250-251	186-188
1-Methylchrysene	[18]	254-255	174-176
4-Methylchrysene	[19]	151	–

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Cyclohexen-1-one (IX). A mixture of 2.1 g of the triene V and 13 g of 2-cyclohexen-1-one (IX) was heated for ten hours at 170° in a glass tube in an atmosphere of carbon dioxide. Fractionation of the reaction mixture yielded 12 g of unchanged cyclohexenone, 0.9 g of the triene V, and 1.7 g of a mixture of the isomeric steroid ketones XXXII in the form of a slightly yellowish viscous liquid, b.p. 137-139° at 0.06 mm; n_D^{20} 1.5420. Neither by standing nor by dissolution in alcohol and cooling could the liquid be caused to crystallize.

Found %: C 83.9, 84.0; H 9.8, 9.85
$C_{19}H_{26}O$. Calculated %: C 84.4; H 9.6

After recrystallization from methanol the semicarbazone melted at 237-237.5° (in a sealed capillary).

Found %: N 13.15; 13.05
$C_{20}H_{29}ON_3$. Calculated %: N 12.84

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with p-Benzoquinone (XI). A mixture of 0.9 g of the triene V and 0.7 g of sublimed p-benzoquinone was dissolved in 15 ml of absolute dioxane and heated in a glass tube in an atmosphere of carbon dioxide for three hours at 65°. The dioxane was distilled off under reduced pressure, and the residue crystallized out, yielding 0.5 g (about 30%) of slightly yellowish crystals of the diketone XXXIII, m.p. 92-105°. After two crystallizations from methanol, well formed crystals were obtained that melted at 108-118° (in a sealed capillary). The melting point did not alter after the first and second recrystallizations; some change evidently took place in the substance when it was melted*.

Found %: C 80.8, 80.9; H 7.9, 7.9
$C_{19}H_{22}O_2$. Calculated %: C 80.85; H 7.8

It was not found possible to obtain either a semicarbazone or a dinitrophenylhydrazone.

Condensation of 3,4,4a,5,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 3,5-Dimethyl-3-cyclopentene-1,2-dione (XII). A mixture of 0.9 g of the triene V, 0.7 g of the dione XII, and 5 ml of dioxane was heated for six hours in a boiling water bath in a glass tube in an atmosphere of carbon dioxide. The dioxane was distilled off, and the residue crystallized out, yielding 0.5 g (about 30%) of the diketone XXXIV, m.p. 92-110°. Two crystallizations from alcohol yielded well-formed yellow crystals of m.p. 100-110°.

Found %: C 80.2, 80.2; H 8.8, 8.8
$C_{20}H_{26}O_2$. Calculated %: C 80.5; H 8.7

---

*Butz and Gaddis [12] give an m.p. of 166-170° for this product.

The extended melting range is no doubt to be explained by the ready isomerization of the diketone XXXIV into the hydroxy ketone XXXV. We have observed such isomerizations in our laboratory in other cases [6].

The isomerization of the diketone XXXIV into the hydroxy ketone XXXV was effected by addition of a drop of piperidine to a solution of 50 mg of the diketone XXXIV in 2 ml of dioxane. After ten minutes the solution was diluted with an equal amount of water, when colorless crystals of the hydroxy ketone XXXV, m.p. 131-132°, separated. They gave a violet coloration with ferric chloride, whereas the original diketone (XXXIV) did not give this reaction.

SUMMARY

1. The complete syntheses of a number of new steroid ketones have been effected by condensation of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-methyl-2-cyclopenten-1-one (VII), 2,4-dimethyl-2-cyclopentene-1-one (VIII), 2-cyclohexen-1-one (IX), 2-methyl-2-cyclohexen-1-one (X), p-benzoquinone (XI), and 3,5-dimethyl-3-cyclopentene-1,2-dione (XII). The steroid ketones obtained by the condensation of the triene V with the cyclopentenones VII and VIII have the so-called "inverted structure, and the main product of the condensation of the triene V with citraconic anhydride has the same structure.

2. It has been shown that displacement of the double bond in the 9(11) position readily occurs when steroid ketones are heated with hydrochloric acid or are shaken in acetic acid solution in presence of a platinum catalyst.

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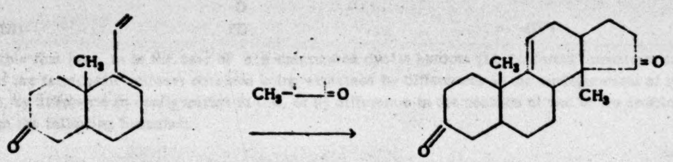
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXIII. SYNTHESIS OF SULFUR ANALOGS OF STEROIDS BY DIENE CONDENSATION OF CYCLIC γ-KETO SULFONES WITH BICYCLIC DIENES

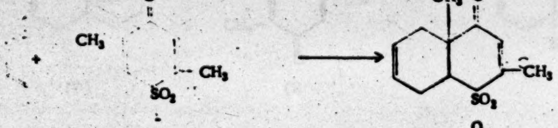
I. N. Nazarov, I. A. Gurvich, and A. I. Kuznetsova

For some years we have been studying in detail the diene condensations of various bicyclic dienes with α,β-unsaturated cyclic ketones with the object of synthesizing polycyclic compounds related to steroids. These syntheses may be illustrated by the example of the diene condensation of 2-methyl-2-penten-1-one with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone:

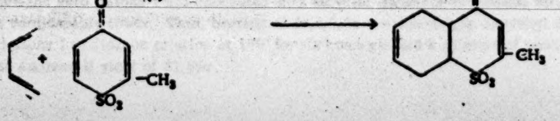


As will be seen from this equation, this method can readily yield various steroid ketones having the so-called "inverted" D ring [1]. As a development of these investigations we decided to study the condensation of bicyclic dienes also with unsaturated cyclic γ-keto sulfones, and so effect the synthesis of sulfur analogs of steroid compounds.

In one of our previous papers we have described the condensation of 1,1-dioxides of 4H-1-thiapyran-4-ones and of dihydro-4H-1-thiapyran-4-ones with 1,3-butadiene [2]. It was then found that the dioxides of substituted 4H-1-thiapyran-4-ones undergo this condensation with greater difficulty than the dioxide of 4H-1-thiapyran-4-one itself. It was established also that the ability of dioxides of substituted 4H-1-thiapyran-4-ones to take part in the diene synthesis depends on the position of the substituent in the nucleus. The introduction of methyl α to the carbonyl makes the diene synthesis appreciably more difficult, but its introduction β to the carbonyl makes the condensation impossible at temperatures of up to 200°. Thus, the 1,1-dioxides of 2,5-dimethyl- and 2-methyl-4H-1-thiapyran-4-ones (I and II) condense with only one molecule of 1,3-butadiene at 200°, good yields of 1,1-dioxides of cis-4a,5,8,8a-tetrahydrothiachromones being obtained:

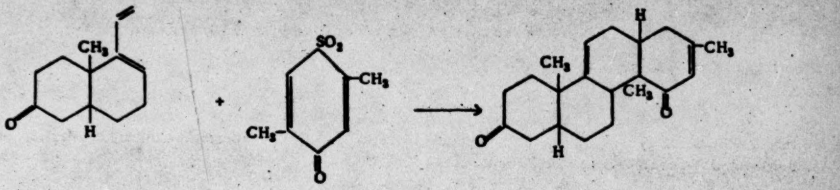


(I)



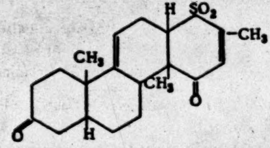
(II)

In this paper we describe the condensation of the unsaturated cyclic γ-keto sulfones I and II with various bicyclic ketones; the products have the skeletons of phenanthro[2,1-bc]thiapyran and flureno[2,1-bc]thiapyran and are sulfur analogs of homosteroids and related compounds. In the condensation of the keto sulfone I with various bicyclic dienes, the components were taken in equimolecular proportions and the reaction was carried out in dioxane solution at 170°; tetracyclic keto sulfones were obtained in 30-70% yield. Thus, heating of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)naphthalenone (III) with the sulfone I in dioxane solution at 170° for 13 hours yielded a mixture of two isomeric tetracyclic diketo sulfones (IV) with an overall yield of 71%:


CH₃
H
O
+
SO₂
CH₃
CH₃
O
H
CH₃
CH₃
CH₃
O
O
H

(III) (I) (IV)

It is probable that here, as in the case of α,β-unsaturated cyclic ketones [1], "inverted" structures are formed, the isomerism of the tetracyclic sulfones obtained being explained by differences in the configurations of substituents at (C-13)-(C-14), by difference in configuration at C-8, or by difference in the position of one of the double bonds, as can be seen from the following formulas: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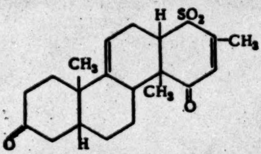
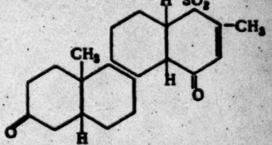
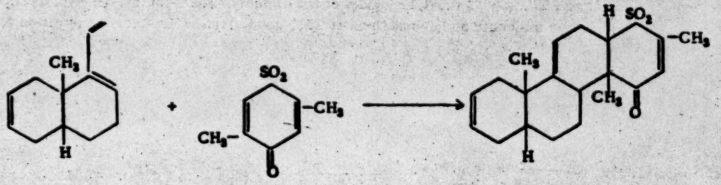
SO₂
CH₃
CH₃
CH₃
O
O
H


H
SO₂
CH₃
CH₃
CH₃
O
O
H

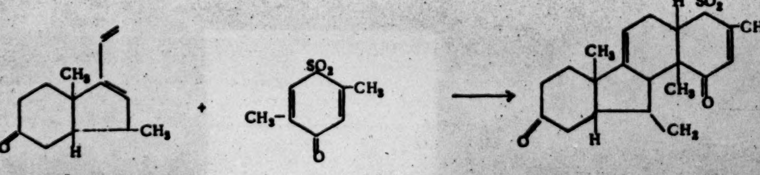

H
SO₂
CH₃
CH₃
H
O
O
H

By condensation of the keto sulfone I with 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) in dioxane solution at 170° for six hours, a mixture of isomeric tetracyclic keto sulfones (VI) was obtained with an overall yield of 60%:


CH₃
H
+
SO₂
CH₃
CH₃
O
H
SO₂
CH₃
CH₃
CH₃
O
H

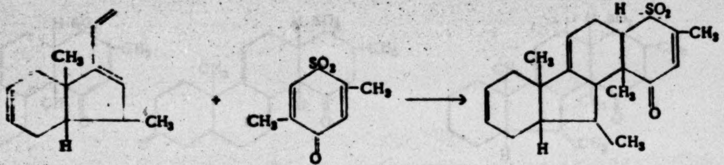
(V) (I) (VI)

When the keto sulfone I was condensed with bicyclic dienes of the indene series, the yield of condensation products was considerably lower. Thus, heating of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (VII) with the keto sulfone I in dioxane solution at 170° for six hours yielded a mixture of isomeric tetracyclic keto sulfones (VIII) with an overall yield of 31.5%:


CH₃
CH₃
O
H
+
SO₂
CH₃
CH₃
O
H
SO₂
CH₃
CH₃
CH₃
O
O
H
CH₃

(VII (I) (VIII)

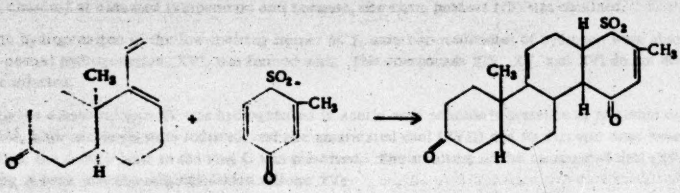
Heating of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (IX) with the sulfone I in dioxane solution at 170° for nine hours yielded a mixture of isomeric tetracyclic keto sulfones (X) with an overall yield of 37%:



(IX) (I) (X)

In all the condensations described, therefore, two isomeric crystalline products were obtained.

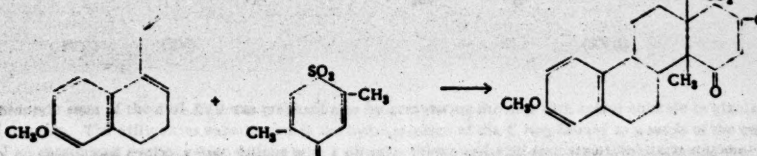
When the diene III was condensed with the keto sulfone II in dioxane solution at 145° for six hours, only one tetracyclic diketo sulfone (XI) was isolated, the yield being 60%:



(III) (II) (XI)

In all of the tetracyclic keto sulfones that we have prepared the A-B and C-D rings are united in the cis-position, since all of these compounds were built up entirely by the diene-condensation method.

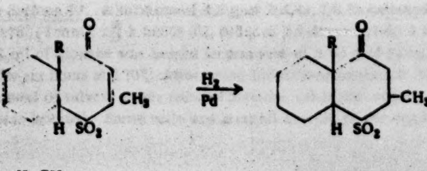
We prepared also the sulfur analog of homoestrone by condensing 3,4-dihydro-6-methoxy-1-vinylnaphthalene (XII) with the keto sulfone I in dioxane solution at 170° for six hours. In this case also we isolated only one tetracyclic keto sulfone (XIII), the yield being 37%:



(XII) (I) (XIII)

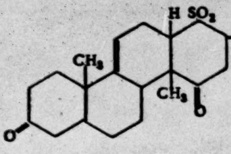
In the methoxy keto sulfone XIII, the C and D rings are united in the cis-position.

As we have shown previously, the products of the diene condensation of 1,3-butadiene with dioxides of substituted 4H-1-thiapyran-4-ones readily take up four atoms of hydrogen in presence of a palladium catalyst [3, 4]:

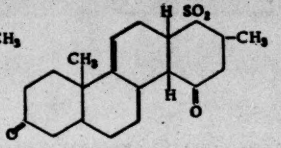


R = H; CH$_3$

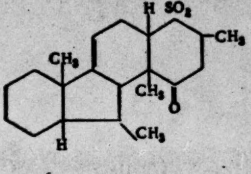
It was found that, when the above-described tetracyclic condensation products were reduced in presence of a palladium catalyst, only the double bonds in rings A and D were hydrogenated, the double bond in ring C formed in the diene condensation being unaffected. Thus, when the isomeric diketo sulfones IV were hydrogenated in presence of a palladium catalyst, only one molecule of hydrogen was absorbed, with formation of the isomeric diketo sulfones XIV. Hydrogenation of the diketo sulfone XI under like conditions yielded the compound XV:



(XIV)



(XV)

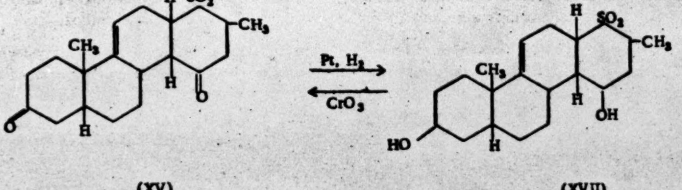


(XVI)

Even when the hydrogenation of the diketo sulfone XI was performed under more severe conditions in presence of palladized charcoal at elevated temperature and pressure, the same product (IV) was obtained.

In the hydrogenation of the low-melting isomer of X, only two molecules of hydrogen were absorbed, and the product of partial hydrogenation, XVI, was formed also. The compounds XIV, XV, and XVI do not decolorize permanganate solution.

When the diketo sulfone XV was hydrogenated in acetic acid solution in presence of platinum oxide and chloroplatinic acid, both carbonyls were reduced, and the unsaturated diol (XVII) and its diacetic ester were obtained. In this case also, the double bond in the ring C was preserved. The structure of the unsaturated diol (XVII) was proved by oxidizing it back into the original diketo sulfone XV:



(XV)

(XVII)

The diacetic ester of the diol XVII was prepared also by acetylating the diol with acetyl chloride in glacial acetic acid solution. The difficulties experienced in the hydrogenation of the C ring formed as a result of the condensation of an unsaturated cyclic γ-keto sulfone with a bicyclic diene, and also data available concerning the shift of such a bond in carbocyclic compounds under the conditions of the diene synthesis [1], give us reason to suggest the possibility of the shift of the double bond in the tetracyclic sulfones described from the 9(11)- to the 8(9)-position. The diketo sulfones XI and XV, like unsaturated bicyclic ketones [3, 4, 5], do not isomerize in presence of sodium methoxide into the corresponding compounds of the trans series.

EXPERIMENTAL

The Tetracyclic Diketo Sulfone IV. A mixture of 4.8 g of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (III) [b.p. 136-138° (7 mm); n_D^{20} 1.5250] [6], 4.3 g of 2,5-dimethyl-4H-1-thiapyran-4-one 1,1-dioxide (I) (m.p. 138-139°) [2], and 15 ml of dioxane was heated in presence of 0.05 g of pyrogallol in a sealed glass tube in an atmosphere of nitrogen for six hours at 170°. After being interrupted overnight, heating was continued for a further seven hours. After removal of solvent under reduced pressure, ether was added, and 6.5 g of crystals of the tetracyclic diketo sulfone IV was isolated. Some resin and a small amount of the original diene remained in the residue. By fractional crystallization from methanol, followed by passage of benzene solutions of the separate fractions through a layer of anhydrous aluminum oxide, it was found possible to isolate 3 g of the low-melting isomer of IV, m.p. 212-213° (in a sealed capillary). The substance crystallized in the form of fine plates.

Found %: C 66.11; 66.21; H 7.29; 7.45; S 8.50
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

In addition, 0.6 g of crystals, m.p. 225-226° (in a sealed capillary), was isolated. This substance crystallized in the form of rosettes; it was the high-melting isomer of IV.

Found %: C 66.54; 66.26; H 7.10; 7.19; S 8.77
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

A mixture of the two isomers melted at 208-218° (softening began at 190°).

The Tetracyclic Keto Sulfone VI. A mixture of 1 g of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) [b.p. 82-84° (2 mm); n_D^{20} 1.5249] [7], 0.99 g of 2,5-dimethyl-4H-1-thiapyran-4-one 1,1-dioxide (I), and 10 ml of dioxane was heated in presence of 0.02 g of pyrogallol in a steel tube for six hours at 170-175°. The solvent was distilled off under reduced pressure, and the residue, after being treated with ether, yielded 1.2 g of crystals, which were separated by fractional crystallization from alcohol into two fractions.

Repeated crystallization of Fraction I (m.p. 192-195°) from alcohol yielded fine silvery crystals of the high-melting isomer of the tetracyclic keto sulfone VI, m.p. 208-209.5°.

Found %: C 69.35; 69.51; H 7.60; 7.65; S 9.12; 9.30
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56 S 9.25

From Fraction II, m.p. 165-178°, crystals of the low-melting isomer of VI were obtained in the form of large oblong prisms, m.p. 182-183°.

Found %: C 69.42; 69.32; H 7.56; 7.59; S 9.62; 9.15
$C_{20}H_{26}O_3S$. Calculated %: C 69.33 H 7.56 S 9.25

The Tetracyclic Diketo Sulfone VIII. A mixture of 0.75 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (VII) (b.p. 108-109°; n_D^{23} 1.5070) [8], 0.75 g of the keto sulfone I, and 8 ml of dioxane was heated in presence of 0.01 g of pyrogallol in a steel tube for six hours at 170-175°. The solvent was distilled off under reduced pressure, and the resin that remained was treated with ether; two fractions of crystals were obtained. From Fraction I (0.25 g, m.p. about 220°) recrystallizations from alcohol and acetone yielded plates of the high-melting isomer of the tetracyclic diketo sulfone VIII, m.p. 235-236°.

Found %: C 66.23; H 7.24; S 8.78
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

The mother liquor yielded 40 mg of the original sulfone.

From Fraction II (0.2 g, m.p. 160-164°) fractional crystallization from alcohol yielded needles of the low-melting isomer of VIII, m.p. 170-171°.

Found %: C 65.95; 66.02; H 7.19; 7.15; S 8.60; 8.68
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

The Tetracyclic Keto Sulfone X. A mixture of 2 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (IX) [b.p. 67-68° (3 mm); n_D^{20} 1.5065] [9], 1.8 g of the keto sulfone I, and 10 ml of dioxane was heated in a glass tube for 4 hours 30 minutes at 170°. Heating, after interruption overnight, was continued for a further 4 hours 30 minutes at 167-170°. The solvent was distilled off under reduced pressure, and ether was added to the residue; 1.4 g of crystals was isolated. Three recrystallizations from alcohol yielded the low-melting isomer of the tetracyclic keto sulfone X in the form of needles, m.p. 158-159° (in a sealed capillary; in an open capillary the substance melted 10° lower).

Found %: C 69.03; H 7.91; S 9.16
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56; S 9.25

In addition, prisms of the high-melting isomer of X, m.p. 172-173° (in a sealed capillary), were isolated.

Found %: C 69.42; H 7.67; S 9.09
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56; S 9.25

The Tetracyclic Diketo Sulfone XI. A mixture of 1.5 g of the diene III [b.p. 125-127° (4 mm); n_D^{20} 1.5250], 1.2 g of 2-methyl-4H-1-thiapyran-4-one 1,1-dioxide (II) (m.p. 141°), and 7 ml of dioxane was heated in presence of 0.03 g of pyrogallol in a glass tube in an atmosphere of nitrogen for six hours at 143-145°. The solvent was distilled off under reduced pressure, and methanol was added to the residue; 2 g of crystals, m.p. about 200°, was isolated. The residue consisted of resin and a small amount of the starting materials. Fractional crystallization from methanol, followed by passage of benzene solutions of the separate fractions through a column of anhydrous aluminum oxide, yielded 1.7 g of the tetracyclic diketo sulfone XI, m.p. 215-215.5° (in a sealed capillary).

Found %: C 65.49; 65.71; H 7.12; 7.00; S 9.31; 9.37
$C_{19}H_{24}O_4S$. Calculated %: C 65.49; H 6.94 S 9.20

After being boiled in methanol solution containing 0.1% of sodium for 15 minutes, the sulfone XI was recovered unchanged. Boiling for two hours caused resinification.

The Tetracyclic Methoxy Keto Sulfone XIII. A mixture of 1.2 g of 3,4-dihydro-6-methoxy-1-vinylnaphthalene (XII) [b.p. 125-132° (0.05 mm); n_D^{18} 1.5805] [10], 1 g of the keto sulfone I (m.p. 138-139°), and 10 ml of dioxane was heated in presence of pyrogallol in a steel tube for six hours at 170-175°. The solution was poured off, and at the bottom of the tube there remained 0.6 g of crystals of the tetracyclic methoxy keto sulfone XIII. The solvent was driven off, yielding a mixture of crystals, from which a further 200 mg of the methoxy keto sulfone XIII was isolated, together with 200 mg of the original sulfone (I) (m.p. 137-138°). A mixed melting point test of the latter and some of the original sulfone gave no depression. The pure tetracyclic methoxy keto sulfone XIII, obtained by recrystallization from benzene, melted at 221-221.5°.

Found %: C 67.12; 67.25; H 6.23; 6.32; S 8.98; 8.86
$C_{21}H_{22}O_4S$. Calculated %: C 67.02; H 6.19 S 8.94

The Tetracyclic Diketo Sulfone XIV. a) A solution of 0.7 g of the low melting isomer of the diketo sulfone IV, m.p. 212-213°, in dioxane was hydrogenated in presence of palladium on a calcium carbonate carrier. The amount of hydrogen absorbed in one hour was 55 ml at 18° and 743 mm (one molecule); hydrogenation was then discontinued. After removal of solvent, two crystallizations from alcohol yielded the diketo sulfone XIV, m.p. 240-241° (in a sealed capillary).

Found %: C 66.04; 65.86; H 7.67; 7.84; S 8.74; 8.76
$C_{20}H_{28}O_4S$. Calculated %: C 65.91; H 7.75; S 8.80

The compound XIV did not decolorize permanganate solution. An attempt was made to hydrogenate the substance IV completely in presence of a palladium catalyst at 100° and also in presence of platinum oxide in a dioxane medium, but in both cases only XIV, m.p. 240-241°, was obtained.

b) A solution of 0.2 g of the high-melting isomer of the diketo sulfone IV, m.p. 224-225°, in a mixture of methanol and benzene was hydrogenated in presence of a palladium catalyst. In the course of 30 minutes about 15 ml (one molecule) of hydrogen was absorbed, and the hydrogenation was discontinued. Two crystallizations from alcohol yielded the second isomer of the diketo sulfone XIV, m.p. 231-232° (in a sealed capillary).

Found %: C 65.91; 65.65; H 7.94; 7.87; S 8.95
$C_{20}H_{28}O_4S$. Calculated %: C 65.91; H 7.75; S 8.80

A mixture with the isomeric sulfone (XIV) (m.p. 240-241°) melted at 205-210°.

The Tetracyclic Diketo Sulfone XV. a) An acetone solution of 0.24 g of the diketo sulfone XI, m.p. 214-215°, was hydrogenated in presence of a palladium catalyst. In the course of 30 minutes about 20 ml (one molecule) of hydrogen at 22° and 753.8 mm had been absorbed; hydrogenation was then discontinued. After removal of acetone and two crystallizations of the residue from methanol, the diketo sulfone XV of m.p. 216-216.5° (in a sealed capillary) was obtained.

Found %: C 64.68; 64.86; H 7.53; 7.53
$C_{19}H_{26}O_4S$. Calculated %: C 65.11; H 7.48

The product (XV) did not decolorize a permanganate solution. A mixture with the original diketo sulfone (XI) melted at 199-200°, with preliminary sintering at 197°. Boiling of the sulfone XV in methanol containing 0.1% of sodium for 30 minutes was without effect, the substance being recovered unchanged Boiling for two hours caused resinification.

b) The diketo sulfone XI of m.p. 214-215° (0.675 g) was hydrogenated in 25 ml of dioxane in presence of 0.5 g of palladized charcoal (10% Pd) in an autoclave at 60 atm and 100-120° for four hours. The solvent was distilled off, and alcohol was added; 0.32 g of a substance was isolated, and this, after recrystallization from alcohol, melted at 209-210°. After passage of a benzene solution of the substance through a column of aluminum oxide, the melting point rose to 215-215.5°. In admixture with the above-described partial-hydrogenation product (XV), no depression of melting point was observed.

The Tetracyclic Keto Sulfone XVI. The diene-condensation product X of m.p. 158-159° (0.3 g) was hydrogenated in dioxane solution in presence of a palladium catalyst until no further hydrogen was absorbed. Recrystallization from alcohol yielded the keto sulfone XVI, m.p. 159-160° (in a sealed capillary).

Found %: C 68.68; 68.43; H 8.68, 8.67; S 9.19; 9.35
$C_{20}H_{30}O_3S$. Calculated %: C 68.49; H 8.63 S 9.15

A mixture of this with the original material melted at 134-142°.

The Tetracyclic Diol XVII. The diketo sulfone XV of m.p. 215-216° (0.28 g) was hydrogenated in 10 ml of glacial acetic acid in presence of platinum oxide and chloroplatinic acid; about 45 ml of hydrogen was absorbed. The acetic acid was distilled off, and benzene was added to the residue; 100 mg of crystals was separated. The benzene solution was passed through an aluminum oxide column; a further 20 mg of crystals together with some clear colorless resin was obtained. Three recrystallizations from benzene yielded the diol XVII, m.p. 245-246° (in a sealed capillary).

Found %: C 67.23; 67.02; H 8.47; 8.51; S 8.00; 7.95
$C_{19}H_{30}O_4S \cdot {}^1/_2C_6H_6$. Calculated %: C 67.13; H 8.26 S 7.96

The diol XVII is readily soluble in alcohol. The colorless glassy resin corresponded in analysis to the diacetic ester of the diol.

Found %: C 62.93; 63.14; H 8.39; 8.24; S 6.90; 6.68
$C_{23}H_{34}O_6S$. Calculated %: C 62.99; H 7.81; S 7.31

Oxidation of the Diol XVII. The diol XVII of m.p. 242-244° (0.065 g) was oxidized with chromic anhydride in glacial acetic acid solution; 0.029 g of chromic anhydride was consumed in the oxidation (about 2 atoms of oxygen per molecule of diol). The acetic acid was distilled off under reduced pressure, and the residue was extracted with benzene, the extract being then passed through an aluminum oxide column. Benzene was distilled off, and a crystalline substance was isolated, which melted, after recrystallization from alcohol, at 214-215°. In admixture with the diketo sulfone XV it showed no depression in melting point.

Acetylation of the Diol XVII. A mixture of 0.1 g of the diol of m.p. 243-244°, 1.5 ml of acetyl chloride, and 1 ml of glacial acetic acid was heated in an oil bath at 110° for 90 minutes (until hydrogen chloride was no longer evolved). The solvent was distilled off under reduced pressure, leaving a residue of clear colorless resin, which was passed, in dioxane solution, through an aluminum oxide column, and then dried for a long time in a vacuum desiccator. It corresponded in analysis to the diacetic ester of the diol XVII.

Found %: C 61.84; 61.94; H 7.84; 7.84; S 7.41; 7.32
$C_{23}H_{34}O_6S$. Calculated %: C 62.99; H 7.81; S 7.31

SUMMARY

1. The tetracyclic keto sulfones IV, VI, and XIII, having the phenanthro[2,1-bc]thiapyran ring system, have been prepared in yields of 70, 61, and 37% respectively by the condensation of the γ-keto sulfone I with the bicyclic dienes III, V, and XII.

2. The tetracyclic keto sulfones VIII and X, having the fluoreno[2,1-bc]thiapyran ring system, have been prepared in yields of 31 and 37% respectively by the condensation of the γ-keto sulfone I with the bicyclic dienes VII and IX.

3. The tetracyclic steroid keto sulfone XI has been prepared in 60% yield by condensation of the cyclic γ-keto sulfone II with the bicyclic diene III.

4. When the tetracyclic keto sulfones IV, X, and XI were hydrogenated in presence of Pd and Pt catalysts, the double bond formed as a result of the diene synthesis was not affected.

5. Hydrogenation of the unsaturated diketo sulfone XV in presence of a Pt catalyst yielded the unsaturated diol XVII.

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**** See Consultants Bureau Translation, page 1449.
***** See Consultants Bureau Translation, page 685.
****** See Consultants Bureau Translation, page 69.
******* See Consultants Bureau Translation, page 955.
******** See Consultants Bureau Translation, page 697.
********* See Consultants Bureau Translation, page 911.
********** See Consultants Bureau Translation, page 977.

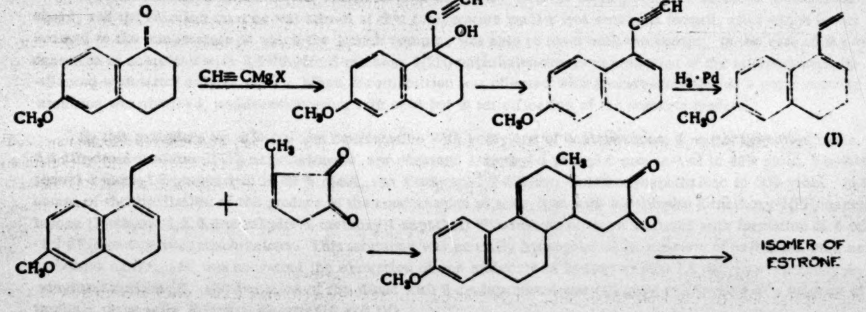
SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

COMMUNICATION XXV. SYNTHESIS OF COMPOUNDS RELATED TO ESTRONE BY THE DIENE-CONDENSATION METHOD

I. N. Nazarov and I. L. Kotlyarevsky

In previous communications from our laboratory [1] we have described a simple method for the synthesis of tetracyclic steroid ketones by the diene condensation of α,β-unsaturated cyclic ketones with bicyclic dienes, such as 1,2,3,4,4a,5,6,8a-octahydro-8-vinylnaphthalene. We have thus prepared a group of steroid compounds related to the male hormones. In continuation of our investigations in this field, we decided to make use of this method for the synthesis of polycyclic ketones related to estrone.

A previous attempt to synthesize compounds of the estrone series has been made by Dane and co-workers [2]. By condensing 1,2-dihydro-7-methoxy-4 vinylnaphthalene with 3-methyl-3 pentene-1,2-dione and then demethylating and reducing the product, Dane succeeded in obtaining an isomer of estrone [3].



For the purpose of this synthesis Dane developed a method for the preparation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) by condensation of ethynylmagnesium halide with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone.

This method is referred to by Goldberg and Muller [4], Bockemuller [5], Anner and Miescher [6], and Heer and Miescher [7], who, however, do not describe their experiments on the preparation of the dihydromethoxyvinylnaphthalene I.

In 1948 Bachmann [8] modified this method, using iodides in place of bromides with benzene as solvent.

Our attempts to repeat the synthesis of 1,2-dihydro-7-methoxy-4-vinylnaphthalene by the procedure described have not been successful. It was found to be quite impossible to effect the condensation of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone with acetylene by Dane's method, and Bachmann's method suffers from the defect that in the course of the distillation of the condensation products, even in a high vacuum (0.01 mm) the material completely resinifies. We have, therefore, developed a new method for the condensation of acetylene with aromatic ketones under pressure. We have observed that at a sufficiently low temperature (−70°) acetylene does not react at all with ethylmagnesium iodide; reaction proceeds at an appreciable rate only at temperatures above −30°. This observation forms the basis of the method we have developed for the condensation of 3,4-dihydro-6-methoxy 1(2H)-naphthalenone with acetylene, which is described in detail in the experimental section. At −70° an ethereal solution of ethylmagnesium bromide (or iodide) will dissolve a large amount of acetylene, but no evolution of ethane is observed.

If the passage of acetylene is carried out at −20°, the reaction proceeds at an appreciable rate, and the ethane evolved rapidly develops a pressure in the reaction vessel which is considerably greater than the pressure of the acetylene itself.

It was found to be most satisfactory to saturate the ethereal solution of ethylmagnesium bromide with acetylene at −70° under a pressure of 2-3 atm, and then carry out the reaction at 0-10°; the pressure in the reaction vessel then rose to 20-30 atm. The "ethynylmagnesium bromide" obtained in this way was a semitransparent reddish-brown viscous mass, which was completely precipitated from ether at −70° and had the appearance of fruit-flavored ice cream. This is evidently the most active form of "ethynylmagnesium bromide", for when a complex of this form is obtained the yields of the reaction products are always greatest. "Ethynylmagnesium bromide" is readily soluble in toluene at temperatures above −4°, but below −4° the toluene solution separates into two layers. The lower layer, which contains the Iotsich complex, is a mobile liquid at temperatures above −20°, but below this temperature it gradually thickens, though it is able to form a fine emulsion with toluene even at −50° when agitated strongly. The nature of our reaction products indicates that our Iotsich complex contained both ethynylmagnesium halide and ethynylbi[magnesium halide], in spite of the fact that the pressure of acetylene during its reaction with ethylmagnesium bromide attained 30 atm.

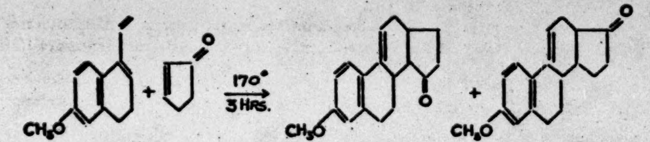
The work of Oddo [9], Iotsich [10], and Salkind and Rosenfeld [11] points to the formation of the monomagnesium compound, ethynylmagnesium halide; but in 1928 Grignard and co-workers [12] published a paper in which they suggested the presence of the equilibrium:

$$XMgC\equiv CMgX + HC\equiv CH \rightleftarrows 2XMgC\equiv CH$$

These authors showed that, when the acetylene Grignard reagent was saturated with acetylene in ether solution for four hours at 1 atm excess pressure at 45°, the subsequent introduction of carbon dioxide into the reaction mixture resulted in a 78% yield of propiolic acid.

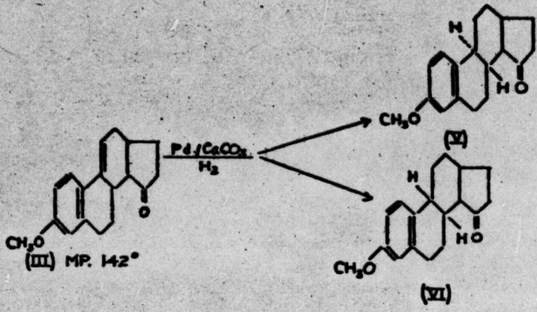
A toluene solution of the ketone was introduced at −50-60° into the Iotsich complex obtained as described above, and the reaction mixture was stirred at that temperature until a fine emulsion formed, after which it was warmed to the temperature at which the Iotsich complex was able to react with the ketone. In the case of the condensation of acetylene with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, decomposition of the complex must be effected with water only at −5-7°. When decomposition was effected with ammonium chloride a nonseparating emulsion was obtained, and decomposition with acid led to resinification of the reaction product.

By this procedure we effected the condensation with acetylene of acetophenone, 4'-methoxyacetophenone, and 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, and obtained 1-methyl-1-phenyl-2-propyn-1-ol in 46% yield, 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol in 30% yield, and 4-ethynyl-1,2-dihydro-7-methoxynaphthalene in 35% yield. In the course of the distillation of the product of the condensation of acetylene with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (1-ethynyl-1,2,3,4-tetrahydro-6-methoxy-1-naphthol) elimination of water occurred with formation of 4-ethynyl-1,2-dihydro-7-methoxynaphthalene. This substance was partially hydrogenated in presence of palladium on a calcium carbonate carrier, and was converted (by absorption of one molecule of hydrogen) into 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I). Condensation of this diene with 2-cyclopenten-1-one (II) gave a 35% yield of a mixture of two isomeric tetracyclic methoxy ketones (III and IV).

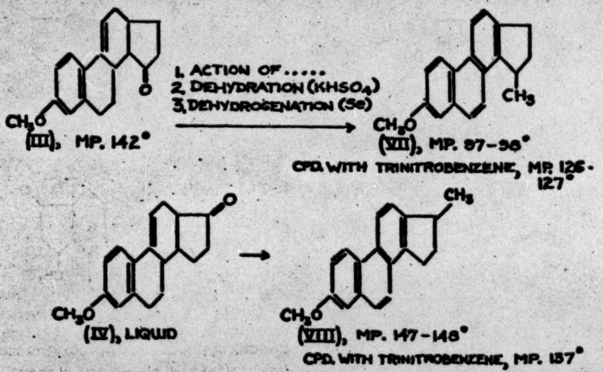


(I) (II) (III) (IV)

The methoxy ketone III was isolated as a crystalline substance, m.p. 142°, but its isomer (IV) was not completely purified and was obtained as light-yellow viscous noncrystallizing oil, b.p. 210-215° (0.05 mm). The crystalline product of m.p. 142° has been described previously by Dane and Eder [13], who erroneously assigned the formula IV to it (methoxy in the 17-position). The formation of the second methoxy ketone (IV) was not observed by Dane and Eder. Hydrogenation of the crystalline methoxy ketone III in presence of a palladium catalyst led to the formation of two isomeric tetracyclic methoxy ketones V and VI, which differ, in all probability, in the configurations of rings B and C:

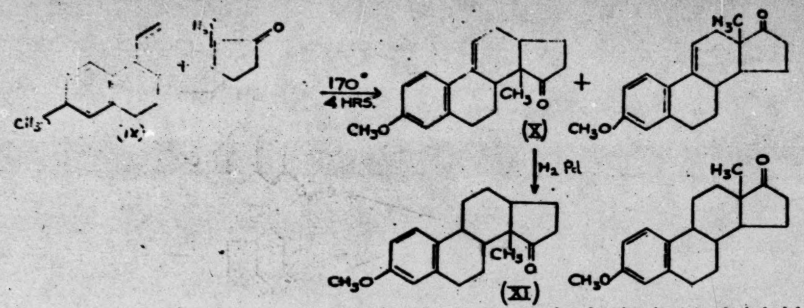

H
H O
CH₃O
(V)
Pd/CaCO₃
H₂
H
H O
CH₃O
(III) MP. 142°
CH₃O
(VI)

The structures of the methoxy ketones III and IV were proved by converting them into known cyclopenta[a]-phenanthrene derivatives (VII and VIII) according to the scheme given below.


CH₃O
(III), MP. 142°
1. ACTION OF .....
2. DEHYDRATION (KHSO₄)
3. DEHYDROGENATION (Se)
CH₃
CH₃O
(VII), MP. 97-98°
CPD. WITH TRINITROBENZENE, MP. 126-127°
CH₃O
(IV), LIQUID
CH₃
CH₃O
(VIII), MP. 147-148°
CPD. WITH TRINITROBENZENE, MP. 137°

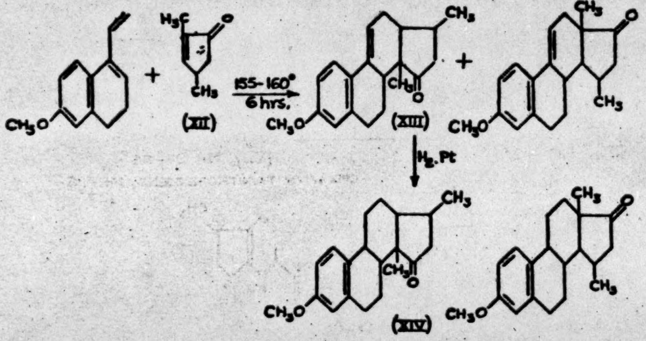
The melting points of the cyclopenta[a]phenanthrene derivatives VII and VIII so obtained, and also of their trinitrobenzene compounds, coincided with the data in the literature [14]. Thus, by the condensation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) with 2-cyclopenten-1-one (II), steroid ketones of both normal and "inverted" structure (keto groups in positions 17 and 15) are formed. As shown in previous communications [15], condensation of bicyclic dienes of the 1,2,3,4,4a,5,6,8a-octahydro-8-vinylnaphthalene type with α,β-unsaturated cyclic ketones yields tetracyclic steroid ketones solely or mainly of "inverted" structure (keto group in the 15-position).

When 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) is condensed with 2-methyl-2-cyclopenten-1-one (IX), the product (X) is again a mixture of isomeric tetracyclic methoxy ketones, and, when this is hydrogenated in presence of a platinum catalyst, one molecule of hydrogen is absorbed and a mixture of isomers of the methyl ether of estrone is formed (XI):

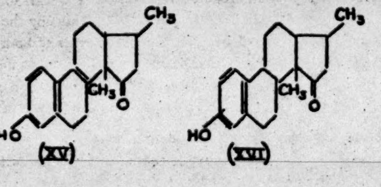

170°
4 HRS.
(IX)
(X)
(XI)
H₂ Pd
CH₃O
CH₃
H₃C
O

In order to elucidate their structure, the methoxy ketones X were reduced with sodium in alcohol, dehydrated, and dehydrogenated over selenium. As a result, a white crystalline substance, m.p. 136-136.3°, was isolated; its compound with trinitrobenzene melted at 147-148°.

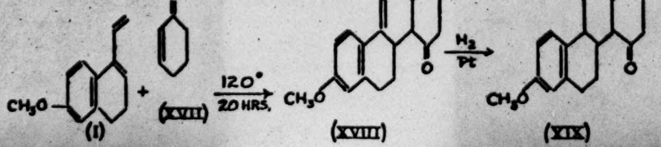
Condensation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) with 2,4-dimethyl-2-cyclopenten-1-one (XII) yielded a mixture of isomeric tetracyclic ketones (XIII), which readily absorbed one molecule of hydrogen when hydrogenated, forming a mixture of isomers (spatial and structural) of the methyl ether of methylestrone (XIV):


155-160°
6 hrs.
(XII)
(XIII)
H₂, Pt
(XIV)
CH₃O
CH₃
H₃C
O

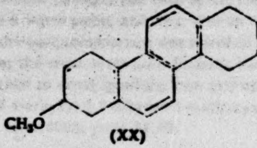
When demethylated with a mixture of glacial acetic and hydrobromic acids, the methoxy ketones XIII and XIV were converted into the corresponding hydroxy ketones XV and XVI, which are isomers of methylestrone:

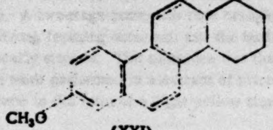

(XV)
(XVI)
HO
CH₃
O

When 1,2-dihydro-7-methoxy-4-vinylnaphthalene was condensed with 2-cyclohexen-1-one (XVII), a 30% yield was obtained of a crystalline methoxy ketone, which probably had the structure XVIII:


120°
20 HRS.
H₂
Pt
(I)
(XVII)
(XVIII)
(XIX)
CH₃O
O

This methoxy ketone, on being hydrogenated, absorbed one molecule of hydrogen and was converted into the crystalline methoxy ketone XIX. Attempts to demethylate the methoxy ketones XVIII and XIX with a mixture of glacial acetic and hydrobromic acids yielded crystalline products having much higher carbon contents than the original compounds. The analytical figures approximated to those for hydrogenated derivatives of methoxychrysene (XX and XXI):


(XX)


(XXI)

1-Methyl-1-phenyl-2-propyn-1-ol and 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol, when partially hydrogenated in presence of palladium on a calcium carbonate carrier, absorbed one molecule of hydrogen and passed into the corresponding propenol compounds. In presence of potassium hydrogen sulfate, 1-methyl-1-phenyl-2-propen-1-ol lost one molecule of water and gave a 60% yield of 2-phenyl-1,3-butadiene. Under the same conditions, 1-p-methoxyphenyl-1-methyl-2-propen-1-ol also lost water, but at the same time polymerized, so that it was not found possible to prepare 2-p-methoxyphenyl-1,3-butadiene by this method. When maleic anhydride was dissolved in an equimolecular amount of 2-phenyl-1,3-butadiene, there was a vigorous reaction with evolution of much heat, and the anhydride of 4-phenyl-4-cyclohexene-1,2-dicarboxylic acid was formed.

EXPERIMENTAL

1,2,3,4-Tetrahydro-6-methoxynaphthalene was prepared by methylation of 2-naphthol and hydrogenation of the 2-methoxynaphthalene obtained in presence of nickel and 1% of acetic acid in alcoholic solution in an autoclave at 140°. The α,β-unsaturated ketones were prepared by the method developed in our laboratory [16].

Oxidation of 1,2,3,4-Tetrahydro-6-methoxynaphthalene to 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone. A solution of 140 g of chromic anhydride in 400 ml of glacial acetic acid and 60 ml of water was added over a period of five hours at 3° to a solution of 140 g of 1,2,3,4-tetrahydro-6-methoxynaphthalene in 800 ml of glacial acetic acid. The mixture was set aside overnight, and the acetic acid was then vacuum-distilled off at a bath temperature of 40-50°. The residual cake was dissolved in 500 ml of water (70°) and set aside overnight. The crystals (90 g) of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone that separated were filtered off, and the filtrate was extracted twice with ether (1 liter in all). The ether extract was dried with magnesium sulfate, and the residue after removal of ether was vacuum-fractionated, yielding 15 g of unchanged tetrahydromethoxynaphthalene, b.p. 83-85° at 1.5 mm, and 20 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in the form of light-yellow crystals, b.p. 130-135° at 1 mm, m.p. 78-79°. The 90 g of crude product was also vacuum-distilled, yielding 16 g of unchanged tetrahydromethoxynaphthalene and 70 g of the dihydromethoxy-1(2H)-naphthalenone, the total yield of which was, therefore, 90 g (76.5% of the tetrahydromethoxynaphthalene that reacted.

Apparatus for Acetylenic Synthesis under Pressure. The apparatus in which the acetylenic syntheses under pressure were carried out consisted of a one-liter steel beaker having a flange; it could be screwed up to a cover, which was firmly clamped in a stand. A stirrer having a three-blade propeller passed through the center of the cover; it was driven with an electric motor and could be rotated at up to 400 r.p.m.. The cover was fitted also with tubes for the entrance and exit of gases, and with a precision manometer reading up to 40 atm in divisions of 0.2 atm. The apparatus was tested with nitrogen at 150 atm. Acetylene was obtained from a cylinder via a reduction valve, and it was passed through a steel washing vessel containing a solution of sodium hydrogen sulfite and through two steel columns filled with granulated caustic soda and calcium chloride respectively before finally passing to the apparatus.

4-Ethynyl-1,2-dihydro-7-methoxynaphthalene. An ethereal solution of ethylmagnesium bromide (20 g of magnesium, 95 g of ethyl bromide, and 200 ml of ether) was cooled to −70° and saturated for 40 minutes with acetylene at a pressure of 2.5 atm. The pressure in the 40-liter cylinder fell by 0.5 atm (absorption of about 20 liters of acetylene). The mixture was gradually warmed to 10° and stirred at that temperature for one hour (the pressure rose to 18 atm). The reaction beaker was again cooled to −70°, and the pressure, then fallen to 4 atm, was released. To the "ethynylmagnesium bromide" so obtained, which had precipitated on the bottom of the beaker in small lumps, a cooled (to −50°) solution of 20 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in 500 ml of absolute toluene was added. The reaction mixture was stirred for 15 minutes at −70°, and was then gradually warmed to

10°, stirred at that temperature for one hour, and then stirred for a further 30 minutes at 45° (pressure 2-3 atm). The product was hydrolyzed by means of ice at −5°, the toluene-ether layer was poured off, and the residue was carefully washed with 200 ml of toluene. The solvent was vacuum-distilled from the united toluene-ether solution. The residue, which crystallized out in the distilling flask, was diluted with ether and filtered, and the residue on the filter was washed with a fresh portion of ether. The product was 7 g of di(3,4-dihydro-6-methoxy-1-naphthyl)acetylene, m.p. 176-177° (from benzene). Ether was removed from the filtrate in a current of nitrogen under reduced pressure, and then at the temperature of a boiling water bath residual solvent was removed, first with a water pump, and then with an oil pump. A two-stage pump was then brought into operation (0.04 mm), and the bath temperature was raised to 140°. Strong foaming occurred, and the bath temperature was maintained at the same level until foaming had practically stopped. The substance was then distilled, precautions being taken to avoid splashing over (all operations were performed in a current of nitrogen). The product was 7.2 g of 4-ethynyl-1,2-dihydro-7-methoxynaphthalene in the form of a light-yellow liquid, b.p. 118-125° (0.04-0.06 mm); n_D^{20} 1.6005; yield 34.5%.

Found %: C 83.30, 83.39; H 7.47, 7.43
$C_{13}H_{12}O$. Calculated %: C 84.75; H 6.52

As already stated by Bachmann, 4-ethynyl-1,2-dihydro-7-methoxynaphthalene is extremely unstable: within 30 minutes of distillation its yellow color had become appreciably more intense, and after standing 12 hours in the air it had become a thick reddish-brown sirup from which it was no longer possible to isolate anything by distillation. It is not recommended that this substance be redistilled, because of the great losses that occur as a result of polymerization. The analytical figures and the somewhat extended boiling range indicate that the 4-ethynyl-1,2-dihydro-7-methoxynaphthalene was contaminated with a small amount (5-10%) of the corresponding acetylenic tertiary alcohol, but when an attempt was made to eliminate water from these residues of tertiary alcohol by distillation of the substance over small amounts of potassium hydrogen sulfate the whole mass quickly polymerized into a hard glassy material, which began to distil in a high vacuum (about 0.01 mm) only at 320°. It is therefore necessary to use 4-ethynyl-1,2-dihydro-7-methoxynaphthalene very soon after its preparation and without further purification.

1,2-Dihydro-7-methoxy-4-vinylnaphthalene. Freshly prepared 4-ethynyl-1,2-dihydro-7-methoxynaphthalene (7.2 g) was hydrogenated in 20 ml of methanol in presence of palladium carried on calcium carbonate. In the course of 90 minutes 900 ml (20°, 752 mm) of hydrogen was absorbed, and the solution then no longer gave a positive test for acetylenic substances with an ammoniacal solution of silver oxide. Fractionation yielded 5.7 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I), b.p. 118-124° at 1.5 mm; n_D^{19} 1.5865. When this substance was ground for two minutes with maleic anhydride, an adduct was formed which, after careful washing with ether, melted at 201-202°, as stated in the literature.

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene with 2-Cyclopenten-1-one. A mixture of 3 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene and 8 g of 2-cyclopenten-1-one (II) (b.p. 34° at 7 mm; n_D^{20} 1.4745) was heated in a sealed tube for three hours at 170°. Vacuum fractionation yielded 6 g of unchanged cyclopentenone (b.p. 35° at 9 mm; n_D^{19} 1.4746) and 2.6 g of condensation product, b.p. 210-215° (0.06 mm). Repeated crystallization from alcohol yielded 1.5 g of the previously described crystalline methoxy ketone III, m.p. 142°, and 0.8 g of a liquid methoxy ketone (IV), b.p. 210-215° (0.5 mm).

Found %: C 80.62, 80.61; H 7.51, 7.59
$C_{18}H_{20}O_2$. Calculated %: C 80.55; H 7.46

The Tetracyclic Methoxy Ketones V and VI. The methoxy ketone III of m.p. 142° (0.7 g) was hydrogenated in 10 ml of methanol in presence of a palladium catalyst at 60°, 70 ml of hydrogen being absorbed in the course of 30 hours. Fractional crystallization from alcohol yielded 60 mg of a tetracyclic methoxy ketone (V or VI), m.p. 160-160.3°.

Found %: C 80.02, 79.80; H 8.32, 8.23
$C_{18}H_{22}O_2$. Calculated %: C 80.01; H 8.15

Also, 200 mg of the second isomer (methoxy ketone V or VI), m.p. 116-117°, was isolated.

Found %: C 79.90, 80.01; H 8.64, 8.67
$C_{18}H_{22}O_2$. Calculated %: C 80.01; H 8.15

Conversion of the Methoxy Ketone III into 16,17-Dihydro-3-methoxy-15-methyl-15H-cyclopenta[a]phenanthrene (VII). A solution of 0.4 g of the methoxy ketone III (m.p. 142°) in 20 ml of absolute ether was added under vigorous stirring to an ethereal solution of methylmagnesium iodide prepared from 0.5 g of magnesium, 3.5 g of methyl iodide, and 40 ml of absolute ether. The mixture was boiled for 30 minutes, treated with 4% hydrochloric acid (17 ml), and extracted with ether. The extract was dried with magnesium sulfate, and the residue after removal of the ether was mixed with 0.5 g of freshly calcined potassium hydrogen sulfate; the mixture was heated in a bath at 180-190° until water ceased to separate (two hours). The product was extracted with ether, and the extract was dried with magnesium sulfate and vacuum-distilled, yielding 0.3 g of a colorless oil, b.p. 190-202° (0.1 mm). Scratching with a rod caused complete solidification (m.p. 88° [from alcohol]). A mixture of 0.28 g of this substance and 0.6 g of selenium was heated in a sealed tube for six hours at 300°. When the mass cooled, complete solidification occurred. The substance was dissolved in hot benzene, filtered three times to remove selenium, and, after removal of benzene, vacuum-distilled: b.p. 160-180° (0.1 mm). The distilled substance was recrystallized: once from a mixture of benzene and alcohol (1:4), and four times from alcohol. The product was 100 mg of 16,17-dihydro-3-methoxy-15-methyl-15H-cyclopenta[a]phenanthrene (VII), m.p. 97-98°; its compound with trinitrobenzene melted at 126-127° (the literature [16] gives 98° and 129° respectively).

Conversion of the Methoxy Ketone IV into 16,17-Dihydro-3-methoxy-17-methyl-15H-cyclopenta[a]phenanthrene (VIII). An ethereal solution of 1.2 g of the methoxy ketone IV (b.p. 210-215° at 0.05 mm) was added under stirring to an ethereal solution of methylmagnesium iodide prepared from 0.5 g of magnesium, 3.5 g of methyl iodide, and 40 ml of absolute ether. The organomagnesium complex was precipitated on the bottom of the flask. The mixture was stirred for one hour at 40°, and then treated first with water (2 ml), and then with 4% hydrochloric acid (17 ml). The product was extracted with ether, and the ether extract was dried with potassium carbonate. The ether was driven off, and the residue was heated with 0.5 g of potassium hydrogen sulfate for two hours at 170° under reduced pressure (8 mm). The dehydration product was extracted with ether, and the ether extract was washed with sodium bicarbonate solution, dried with magnesium sulfate, and vacuum-distilled, yielding 0.7 g of a light-yellow oil, b.p. 180-200° at 0.06 mm, which was heated with 0.5 g of selenium in a sealed tube for three hours at 300-320°. On cooling the substance solidified completely. When the tube was opened an appreciable pressure of hydrogen selenide was noted. The crystalline solid was dissolved in hot benzene, and the benzene solution was diluted with an equal volume of alcohol; suspended selenium was carefully filtered off. When the filtrate was cooled, a voluminous crystalline precipitate appeared. Four recrystallizations from alcohol yielded 200 mg of 16,17-dihydro-3-methoxy-17-methyl-15H-cyclopenta[a]phenanthrene (VIII), m.p. 147-148°; compound with trinitrobenzene, m.p. 136.5-137° (the literature [16] gives 147.5-148° and 137° respectively).

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2-Methyl-2-cyclopenten-1-one (IX). A solution of 1 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) in 10 g of 2-methyl-2-cyclopenten-1-one (IX) (b.p. 62-65° at 23 mm; n_D^{20} 1.4795) was heated for four hours in a sealed glass tube at 170°. After removal of methylcyclopentenone and an intermediate fraction (0.6 g, b.p. 110-140° at 2 mm) by distillation, 0.6 g of a mixture of steroid methoxy ketones (X) was isolated as a light-yellow glassy substance, b.p. 220-222° at 2 mm.

Found %: C 80.32, 80.04; H 8.12, 8.01

$C_{19}H_{22}O_2$. Calculated %: C 80.84; H 7.80

Chromatographic separation on aluminum oxide was carried out with 1 g of this product, and elution with petroleum ether yielded 0.3 g of material, which was dissolved in 15 ml of alcohol and reduced with sodium (1 g) at 78°. The mixture was neutralized with 4 ml of concentrated hydrochloric acid, the alcohol was distilled off, and the substance was extracted with ether. The ether extract was dried with magnesium sulfate, and the residue after removal of ether was heated for one hour with 0.5 g of freshly calcined potassium hydrogen sulfate at 180°. The product was extracted with ether, and the ether extract was washed with sodium bicarbonate solution, dried with magnesium sulfate, and vacuum-distilled, yielding 0.2 g of a light-yellow oil, b.p. 180-195° (0.2 mm). This dehydrogenation product was heated with 93 mg of selenium in a sealed tube at 320-330° for seven hours. The substance was freed from resinous contamination by chromatography on aluminum oxide and recrystallized several times from alcohol, yielding 50 mg of colorless crystals, m.p. 136-136.3°.

Found %: C 86.58, 86.54; H 6.49, 6.35

$C_{19}H_{18}O$. Calculated %: C 87.02; H 6.87

Its compound with trinitrobenzene melted at 147-148° (from alcohol).

Hydrogenation of the Steroid Methoxy Ketones X. The substance (0.27 g) was hydrogenated in 20 ml of alcohol in presence of a platinum catalyst; 22 ml of hydrogen (one molecule) was absorbed. The alcohol was driven off, and the substance was vacuum-distilled, yielding 220 mg of a light-yellow oil, b.p. 199-203° at 0.1 mm. The product was a mixture of isomers (XI) of the methyl ether of estrone.

Found %: C 80.42, 80.26; H 8.01, 8.03

$C_{19}H_{24}O_2$. Calculated %: C 80.20; H 8.44

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2,4-Dimethyl-2-cyclopenten-1-one (XII). A mixture of 2.7 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) and 8 g of 2,4-dimethyl-2-cyclopenten-1-one (XII) was heated in a sealed tube for six hours at 155-160°. Unchanged dimethylcyclopentenone was driven off under reduced pressure, and fractionation of the residue yielded 0.8 g of a mixture of the steroid methoxy ketones (XIII) as very viscous yellow oil, b.p. 205-208° (0.1 mm).

Found %: C 80.04, 80.21; H 8.01, 8.16
$C_{20}H_{24}O_2$. Calculated %: C 81.04; H 8.1

Demethylation of the Steroid Methoxy Ketones XIII. A mixture of 0.4 g of material, 5 ml of glacial acetic acid, and 3 ml of 48% hydrobromic acid was heated under reflux for six hours at a bath temperature of 120°. The acids were driven off under reduced pressure, and the residue was dissolved in 20 ml of 3% caustic soda. The alkaline solution was extracted with ether and acidified with hydrochloric acid. A mixture of the steroid ketones XV (0.2 g) was isolated in the form of a yellow glassy mass, b.p. about 215-220° (0.03 mm).

Found %: C 81.36, 81.31; H 7.67, 7.77
$C_{19}H_{22}O_2$. Calculated %: C 80.84; H 7.80

Hydrogenation of the Steroid Ketones XIII. A solution of 0.75 g of the substance in 20 ml of alcohol was hydrogenated in presence of platinum, one molecule of hydrogen (64 ml, 20°, 745 mm) being absorbed in two hours. Vacuum fractionation yielded 0.65 g of the mixture of steroid methoxy ketones XIV in the form of a colorless oil, b.p. 195-200° (0.1 mm).

Found %: C 80.23, 80.33; H 8.61, 8.81
$C_{20}H_{26}O_2$. Calculated %: C 80.45; H 8.72

Demethylation of the Steroid Methoxy Ketones XIV. A mixture of 0.23 g of the substance, 3 ml of glacial acetic acid, and 1.5 ml of 48% hydrobromic acid was boiled for three hours, the bath temperature being 120-125°. The acids were distilled off under reduced pressure, and the residue was dissolved in 10 ml of 5% caustic potash. The alkaline solution was washed with ether and acidified with hydrochloric acid. An amorphous solid mass was precipitated, and this, after being filtered off, washed with water, and dried, was vacuum-distilled, yielding 0.17 g of the mixture of steroid hydroxy ketones XVI in the form of light-yellow glassy substance, b.p. 215-220° (0.03 mm).

Found %: C 80.40, 80.17; H 8.54, 8.64
$C_{19}H_{24}O_2$. Calculated %: C 80.20; H 8.44

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2-Cyclohexen-1-one (XVII). A solution of 4 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) in 12 ml of 2-cyclohexen-1-one (XVII), b.p. 161°; n_D^{20} 1.4860 was heated in a sealed tube for 20 hours at 120°. The cyclohexeneone was distilled off under reduced pressure, and was followed by 2 g of a substance boiling over the range 100-170° at 1 mm. Alcohol (20 ml) was added to the residue in the flask, and the solution was set aside for a day. The crystals that separated were filtered off. Recrystallization from alcohol yielded 2 g of the tetracyclic methoxy ketone XVIII in the form of glistening white crystals, m.p. 132°.

Found %: C 80.80, 81 09; H 7 93, 7.74
$C_{19}H_{22}O_2$. Calculated %: C 80.84; H 7 80

Hydrogenation of the Methoxy Ketones XVIII. The substance XVIII of m.p. 132° (0.3 g) was hydrogenated in 20 ml of alcohol in presence of a palladium catalyst, first at room temperature, and then at 70°; 23 ml of hydrogen was absorbed The product was distilled off at 220-222° (0.1 mm), left for a week to crystallize, and then recrystallized from alcohol. The product was 70 mg of the tetracyclic methoxy ketone XIX in the form of white crystals, m.p. 147° (from alcohol).

Found %: C 80.05, 79.81; H 9.24, 9.27
$C_{19}H_{24}O_2$. Calculated %: C 80.20; H 8.44

Demethylation of the Methoxy Ketones XVIII. A mixture of 0.1 g of the substance, 6 ml of glacial acetic acid, and 3 ml of 48% hydrobromic acid was boiled for three hours (bath temperature 120°) When the mixture was cool, crystals came down, and these were separated and recrystallized from 60% alcohol, yielding 50 mg of 1,2,3,4-tetrahydro-8-methoxychrysene (XX) in the form of gray crystals melting at 183° (from 60% alcohol), insoluble in dilute alkali.

Found %: C 86.91; H 7.48
$C_{19}H_{18}O$. Calculated %: C 87.05; H 6.88

Demethylation of the Methoxy Ketones XIX. A mixture of 40 mg of the substance, 2 ml of glacial acetic acid, and 1 ml of 48% hydrobromic acid was boiled for 90 minutes (bath temperature 120-130°) When the mixture was cooled, crystals separated, and these, after recrystallization from 70% acetic acid, washing with water, and drying in a vacuum desiccator over sulfuric acid, melted at 219-220°. In this way 30 mg of pinkish crystals were obtained, evidently of 1,2,3,4,4a,12a-hexahydro-8-methoxychrysene (XXI); they were insoluble in dilute alkali.

Found %: C 86.32, 86.37; H 6.46, 6.63
$C_{19}H_{20}O$. Calculated %: C 86.40; H 7.57

SUMMARY

1. A new method has been developed for the preparation of ethynylmagnesium bromide under pressure, and it has been condensed with aromatic and hydrogenated aromatic ketones. In this way the synthesis has been effected in 30-46% yield of 1-methyl-1-phenyl-2-propyn-1-ol, 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol, and 4-ethynyl-1,2-dihydro-7-methoxynaphthalene.

2. The last compound has been selectively hydrogenated to 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I), which has been condensed with 2-cyclopenten-1-one (II), 2-methyl-2-cyclopenten-1-one (IX), 2,4-dimethyl-2-cyclopenten-1-one (XII) and 2-cyclohexen-1-one (XVII). In this way a number of tetracyclic ketones related to estrone have been synthesized, and in two cases their structures have been proved.

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STABILITY OF SKELETAL NICKEL CATALYST AT ELEVATED TEMPERATURE

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The skeletal (i.e., Raney) nickel catalyst has found application mainly in low-temperature hydrogenation reactions, and is scarcely used for processes, e. g. dehydrogenation, requiring higher temperatures. The limited field of application of this catalyst is evidently the result of its inadequate thermal stability.

The available data on the thermal dehydrogenation and thermal stability of the skeletal nickel catalyst are contradictory. According to Aubry [1], when Raney nickel is boiled in concentrated sodium or potassium carbonate solution for a long time, much of its adsorbed hydrogen is removed, and aggregation of its particles occurs; the catalyst becomes darker in color, changes in specific volume, and partially loses its activity. Bougault and coworkers [2] have shown that, in a vacuum, dehydrogenation of skeletal nickel begins at 100° and is complete at 250°. Mozingo [3] effected the removal of hydrogen from skeletal nickel suspended in a high-boiling organic substance (dibutyl phthalate) by passage of carbon dioxide at 220°. Schwab and Zorn [4] observed that, when skeletal nickel was kept in a high vacuum for five days at room temperature, its catalytic activity was greatly reduced. We gain the impression that the skeletal nickel catalyst is of low thermal stability and is already fully dehydrogenated and deactivated at temperatures of 200-250°.

Other facts, however, point to the appreciable stability of this catalyst, even at elevated temperatures: Rutovsky and coworkers [5] have dehydrogenated borneol to camphor at 240° in its presence, and Rappoport [6] has used it in the dehydrogenation of cyclohexane and methylcyclohexane

It is also not clear whether the deactivation of this catalyst at high temperature is due to recrystallization or to the effect of other factors.

As Eucken has shown [7], the specific surface of a skeletal nickel catalyst falls only slowly during the activation process, even when a comparatively high temperature is used:

Temperature of catalyst activation (°C)	25	200	370
Specific surface (sq. m/g)	22.9	18.5	16.4

It may therefore be supposed that sintering is not the main cause of the deactivation of this catalyst under the usual conditions of the hydrogenation or dehydrogenation process.

It has recently been established that the skeletal nickel catalyst is a metal-hydrogen system. Hydrogen is an essential component of its active surface. Hence, not only blocking of the active surface, but also dehydrogenation of the catalyst must constitute an important deactivation process.

In view of these considerations we have investigated the thermal stability of a skeletal nickel catalyst. The results show that the catalyst is very stable in absence of hydrogenatable substances. At 300° its activity was unaltered, and only when baked at 400° did its activity begin to fall; but even after it was baked at 500° and 570° it still had a considerable activity and retained a large amount of hydrogen. Under vacuum conditions the catalyst was deactivated at a lower temperature, and the dehydrogenation and deactivation of Raney nickel observed by some investigators at 200-250° can be explained by the effect of the vacuum and of such contaminants as sodium and potassium carbonates and dibutyl phthalate. On the other hand, borneol and cyclohexane and their dehydrogenation products have little effect on the activity of the catalyst.

The apparent contradictions in the facts given above are therefore explained: the stability of the skeletal catalyst is affected mainly not by the temperature, but by the nature of the process and the chemical nature of the substances whose reactions are being accelerated by the catalyst.

EXPERIMENTAL

Thermal Deactivation of Skeletal Nickel Catalyst in a Current of Nitrogen

The catalyst was prepared by treating a 50% Ni–Al alloy with 20% caustic soda at 100°. The active catalyst (15 g) in the form of a paste was placed in a quartz tube, which was heated in an electric furnace fitted with a thermoregulator. A current of nitrogen freed from oxygen and moisture by means of sodium dithionite and sulfuric acid respectively was passed continuously during the experiment at 3.5 l/hour. The preliminary heating of the furnace to the temperature of the experiment did not, as a rule, take more than 30-40 minutes, and it was not included in the time given for the duration of the experiment. At the end of the experiment, the catalyst was cooled to room temperature and then transferred in a current of nitrogen to below the surface of water in a suitable vessel.

The activities of the original and thermally deactivated samples of catalyst were estimated from measurements of the rate of hydrogen absorption in the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20°.

TABLE 1

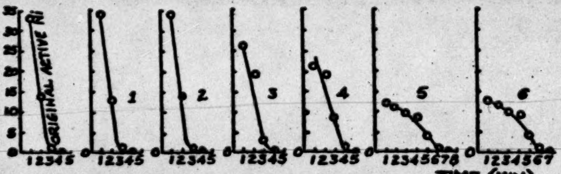
Thermal Deactivation of a Skeletal Nickel Catalyst in a Current of Nitrogen

Temperature (°C)	Duration of expt. (hr)	Activity of 1 g of catalyst in the first 4 min. of the hydrogenation of phenyl vinyl ether (rate of hydrogen absorption in ml/min)	Amount of hydrogen found in 1 g of catalyst (ml)
200	2	33.6–12.8–1.0 –0.2	–
300	2	33.7–13.5–0.9 –0.2	80
300	4	29.4–16.5–2.0 –0.5	–
400	2	26.2–18.3–3.2 –0.2	–
500	2	20.9–18.9–8.7 –0.9	63
570	2	12.4–11.1–9.7 –7.3	54
570	6	12.6–11.5–10.1–8.9	–
Original active nickel		33.0–13.7–1.2 –0.2	179

Before the activity determination, the catalyst was saturated with hydrogen for 15 minutes. A determination was made also of the residual hydrogen in the catalyst by treating it with excess of a 3% solution of p-benzoquinone in dioxane in an atmosphere of nitrogen for one hour at 60°.

It follows from Table 1 and Fig. 1 and 2 that the skeletal nickel catalyst preserved its original activity after a two-hour heating at 300°. After two hours at 400°, the activity of the catalyst fell appreciably. Considerably greater deactivation occurred at 500°, and it was still greater at 570°.

These results show that only at 400° and above does appreciable deactivation occur. The effect increases with rise in temperature, but even after being baked at 570° the catalyst still retains much of its activity and



Ordinates: Rate of H_2 adsorption (ml/min

Fig. 1. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a current of nitrogen: 1) at 200°, 2 hr; 2) at 300°, 2 hr; 3) at 400°, 2 hr; 4) at 500°, 2 hr; 5) at 570°, 2 hr; 6) at 570°, 6 hr.

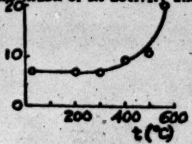


Fig. 2. Half-life of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a current of nitrogen for two hours at a temperature in the range 200-570°.

TABLE 2
Thermal Deactivation of a Skeletal Nickel Catalyst in a Vacuum

Temperature (°C)	Duration of expt. (hr)	Activity of 1 g of catalyst in the first 4 min. of the hydrogenation of phenyl vinyl ether (rate of hydrogen absorption in ml/min)	Amt. of hydrogen found in 1 g of catalyst (ml)
300	2	17.2 − 16.3 − 12.7 − 2.8	52
400	2	15.3 − 14.3 − 11.8 − 5.3	40
Original active nickel		26.8 − 14.6 − 2.2 − 0.7	207

contains an appreciable amount of hydrogen. Increase of the duration of thermal treatment at 570° from two to six hours has no effect on the reduction in the activity of the catalyst.

It is necessary to draw attention to another interesting fact. It has been found previously that about 70% of all the hydrogen contained in the catalyst is a constituent part of its active surface, and only about 30% of the hydrogen can be removed without effect on the activity of the catalyst [9]. In the experiments on thermal deactivation in a current of nitrogen at 300°, the catalyst was found to contain about 50% of the amount of hydrogen normally found in an untreated sample of catalyst, and yet the activity of the catalyst was fully retained. The activating effect of hydrogen in a catalyst that has been submitted to thermal treatment is therefore considerably higher than in a freshly prepared catalyst.

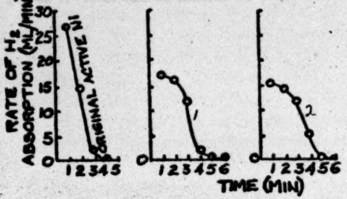


Fig. 3. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a vacuum for two hours: 1) at 300°; 2) at 400°.

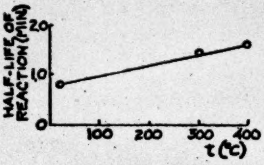


Fig. 4. Half-life of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a vacuum for two hours at 300° and 400°.

Thermal Deactivation of Skeletal Nickel Catalyst in a Vacuum

Active catalyst (10 g) in the form of a paste was transferred in a current of hydrogen to a quartz tube. One end of the tube was securely stoppered, and the other was attached to a vacuum pump that maintained a pressure of 1-5 mm Hg in the system. In other respects the experiment was performed like those on thermal deactivation in a current of nitrogen. The results obtained are given in Table 2 and represented in Figs. 3 and 4. It follows from Table 2 and Figs. 3 and 4 that in the thermal-deactivation treatments in a vacuum at 300° and 400° the activity and hydrogen content of the catalyst fall more rapidly than in treatments carried out in a current of nitrogen.

SUMMARY

1. An investigation has been made of the thermal deactivation of a skeletal nickel catalyst in a current of nitrogen and in a vacuum.

2. It has been shown that a skeletal nickel catalyst is of good stability to baking in a current of nitrogen in absence of organic substances. Its activity is not reduced by a two-hour baking at 300°; deactivation and dehydrogenation of the catalyst become appreciable only at 400° and higher, and they then become more and more marked as the temperature is raised.

3. When the catalyst is heated in a vacuum, its activity falls more rapidly than when treatment is carried out in a current of nitrogen.

4. The results obtained support our hypothesis that the most important cause of the loss in the activity of skeletal nickel catalyst under the usual conditions of hydrogenation is not recrystallization, but destruction of the active surface by chemical dehydrogenation and blocking.

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MACROMOLECULAR COMPOUNDS

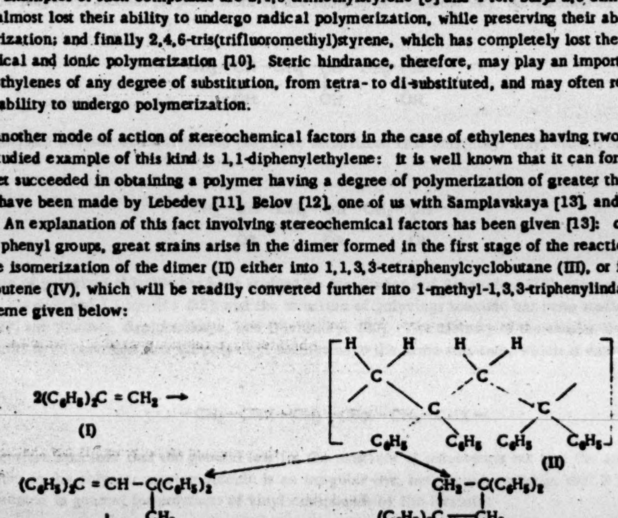
COMMUNICATION 60. ROLE OF STEREOCHEMICAL FACTORS IN THE POLYMERIZATION PROCESS

V. V. Korshak and N. G. Matveeva

In previous communications [1-5] we have given the results of investigations on the effect of substituents in the ethylene molecule on its polymerizability. On the basis of the behavior of halogen-substituted ethylenes [1], certain 1,1-diarylethylenes [2], ar-substituted styrenes [3, 4] and α-methylstyrenes [5], we have succeeded in proving the correctness of the hypothesis that we have advanced, according to which the polymerizability of substituted ethylenes is determined by the number and sizes of the substituents [6-8].

Stereochemical factors are therefore of the greatest importance in the large group of tri- and tetra-substituted ethylenes, since it is in these that steric hindrance due to the substituents is of most significance [1]. We have, however, succeeded in showing that even for mono- and di-substituted ethylenes stereochemical factors are extremely important. First of all, we have unsymmetrical disubstituted ethylenes such as 2,6-dimethoxy-α-methylstyrene [5] and 4-tert-butyl-α,2,6-trimethylstyrene [5], which have completely lost their tendency to polymerize owing to the complete screening and blocking of the double bond by the substituents The same sort of phenomenon is found in monosubstituted ethylenes when the substituent is sufficiently ramified and so able to block the vinyl group. Examples of such compounds are 2,4,6-trimethylstyrene [9] and 4-tert-butyl-2,6-dimethylstyrene [3], which have almost lost their ability to undergo radical polymerization, while preserving their ability to undergo ionic polymerization; and finally 2,4,6-tris(trifluoromethyl)styrene, which has completely lost the ability to undergo both radical and ionic polymerization [10]. Steric hindrance, therefore, may play an important role in the behavior of ethylenes of any degree of substitution, from tetra- to di-substituted, and may often result in complete loss of the ability to undergo polymerization.

We meet another mode of action of stereochemical factors in the case of ethylenes having two large substituents. A well-studied example of this kind is 1,1-diphenylethylene: it is well known that it can form a dimer, but no one has yet succeeded in obtaining a polymer having a degree of polymerization of greater than 2, although attempts have been made by Lebedev [11], Belov [12], one of us with Samplavskaya [13], and other investigators [14]. An explanation of this fact involving stereochemical factors has been given [13]: owing to the large size of the phenyl groups, great strains arise in the dimer formed in the first stage of the reaction which lead to the immediate isomerization of the dimer (II) either into 1,1,3,3-tetraphenylcyclobutane (III), or into 1,1,3,3-tetraphenyl-1-butene (IV), which will be readily converted further into 1-methyl-1,3,3-triphenylindan (V), as shown in the scheme given below:



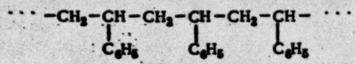
In this case, therefore, stereochemical factors play an important part in the actual polymerization process; they lead to the early rupture of the chain [7]. There is reason to suppose that this is not an isolated case, for it is known that many monomers having two substituents in the 1,2-positions tend to form dimers; these include stilbene [15], 1,2-dichloroethylene [16], and cinnamic acid [17]. The mechanism whereby the chain is terminated is probably similar for these compounds.

It may be supposed that stereochemical factors, apart from having effects of these two types, have some influence on the courses of the separate elementary reactions of the polymerization process, thus determining a number of the characteristics of the process and the structure of the polymer that have been previously attributed entirely to polar effects — primarily, to the polarization of the monomer.

The elucidation of all the details and the building up of a complete picture of stereochemical effects in polymerization processes comprise a task demanding much investigational work and a considerable period of time. Even now, however, it is possible to present certain sides of the question sufficiently clearly and with reasonable confidence in their accuracy.

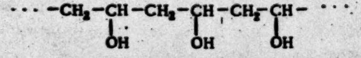
In this paper we shall consider the question of the extent to which stereochemical factors determine the manner in which the monomer residues are arranged along the macromolecule of the polymer. It has been generally considered that the directions in which the monomer residues are disposed in the polymer chain are determined by the polarization of the double bond, as a result of which the residues take up definite directions along the chain.

Investigations by many workers have shown that monomer molecules take up a head-to-tail arrangement in the polymer macromolecule. Thus, Staudinger and Steinhofer [18] and Midgeley [19] have shown that the polystyrene molecule has this structure, its formula being:



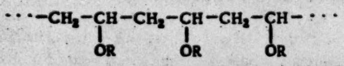
$$\cdots-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-\cdots$$

The structure of polyvinyl acetate has been studied by Staudinger and Schwalbach [20], Marvel and Denoon [21], Korshak and Zamyatina [22], and Losev and Trostyanskaya [23], and they have found that both polyvinyl acetate itself, and also polyvinyl alcohol prepared from it, are built up in the same way, the formula of the latter being as follows:



$$\cdots-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\cdots$$

Chalmers [24] and Korshak and Zamyatina [25] have established that poly[alkyl vinyl ethers] have the following structure:



$$\cdots-CH_2-\underset{OR}{\underset{|}{CH}}-CH_2-\underset{OR}{\underset{|}{CH}}-CH_2-\underset{OR}{\underset{|}{CH}}-\cdots$$

The structure of polyvinyl chloride has been studied by Staudinger and Schneiders [26], Marvel, Sampel, and Roy [27], and Korshak and Zamyatina [28]; and the structure of polyvinyl bromide has been studied by Ostromyslensky [29] and Korshak, Samplavskaya, and Dovolskaya [30]. The identity of the results obtained in the two cases permits us to conclude that all polyvinyl halides have the same structure, which is expressed by the formula:

$$\cdots-CH_2-CHX-CH_2-CHX-CH_2-CHX-\cdots$$

We may therefore conclude that the general law for the structure of polymers is not that the arrangement of monomer residues in the polymer macromolecule is an irregular one, but, on the contrary, that it is regular, and may be represented in general for polymers of vinyl compounds by the formula:

$$\cdots-CH_2-CHX-CH_2-CHX-CH_2-CHX-\cdots$$

and for polymers of vinylidene compounds by the formula:

$$\cdots-CH_2-CX_2-CH_2-CX_2-CH_2-CX_2-\cdots$$

The explanation advanced for this is that the double bond of the monomer is polarized, so that each carbon atom has a charge:

$$\overset{\ominus}{CH_2} = \overset{\oplus}{C}HX,$$

and the monomer residues have to unite through oppositely charged carbon atoms [31]. Recently, this concept has been further supplemented by the idea of the positive or negative charge of the double bond, which is regarded as affecting the ease with which different monomers combine in copolymerization [32].

We consider that these concepts should be supplemented by taking into account the effect of the stereochemistry of the monomer on the polymerization process. In principle, the uniting of two molecules, as we have already noted, can proceed in two ways: head to head, or head to tail. In practice, only one method is realized: head to tail. This method of uniting monomer molecules is to be preferred also from the stereochemical point of view: it is only necessary to compare the two methods of uniting monomer residues, in the case, for example, of the polymerization of vinylidene chloride, for the difference between them to become clear. In the case of head-to-head union, two vinylidene chloride molecules will combine as follows:

$$CH_2 = CCl_2 + CCl_2 = CH_2$$

and yield a macromolecule of the following structure:

$$\cdots -CH_2-CCl_2-CCl_2-CH_2- \cdots$$

In the case of head-to-tail union, the positions of the uniting molecules will be different, and the structure of the polymer will also be different:

$$CH_2 = CCl_2 + CH_2 = CCl_2$$

$$\cdots -CH_2-CCl_2-CH_2-CCl_2- \cdots$$

In the first case, therefore, the two groups $= CCl_2 + CCl_2 =$, have to unite, which is precisely analogous to the case, which we have investigated, of the polymerization of tetrachloroethylene, which is quite unable to polymerize, as we have already established [1]. The source of the inertness of tetrachloroethylene lies, as we have shown, in the great steric obstacles that are met in the union of two $= CCl_2$ groups. These great steric obstacles make it impossible for tetrachloroethylene to polymerize, and they also do not permit vinylidene chloride molecules to unite in such a stereochemically difficult manner.

In the second case it is the groups $= CH_2$ and $= CCl_2$ that have to unite, and this, of course, does not demand the surmounting of such great steric obstacles; it should therefore proceed with considerably greater ease. In the actual polymerization, therefore, the vinylidene chloride molecules unite in the second way. It will be clear that the activation energy in the first case will be much greater than in the second, in which the obstacles to be surmounted are not so great.

We meet similar behavior in practically all monomers, which are generally vinyl or vinylidene compounds. Thus, also in the case of vinyl compounds we find great stereochemical differences between the two possible modes of union of monomer molecules. In the case of vinyl chloride, for example, in the first case the groups $= CHCl + + CHCl =$ must unite, but in the second the groups $= CHCl + CH_2 =$. It will be clear that in the first case the steric hindrance will be much greater than in the second, and this fact determines the method of union that is observed in practice. In the first case we see the same picture as that presented by dichloroethylene, which, as is well known, does not polymerize, as a result, we consider, of steric-hindrance effects, together with other causes relating to polar effects.

SUMMARY

1. The part played by stereochemical factors in polymerization processes has been examined, and it has been shown that they may play an important part, not only in the first stages of the reaction, which determine the existence or nonexistence of polymerizability, but also in the succeeding stages of the process.

2. It has been shown that in the polymerization process stereochemical factors can cause the chain to be terminated at the dimer stage; this is a consequence of the great strains that may arise in the molecule on account of the presence of bulky substituents.

3. It has been shown that stereochemical factors play an important part, together with polar effects, in determining the directions in which the monomer molecules unite when forming the polymer chain, the directions being determined by the magnitudes of the steric hindrance effects operating for the two different ways of building up the macromolecule.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 63. POLYESTERS OF 1,20-EICOSANEDIOL

V. V. Korshak and S. V. Vinogradova

Up to now only isolated attempts have been made to determine how the physical properties of a polymer depend on the length of the structural unit, i.e., of the monomer. Hill and Walker [1], for example, give a graph showing the variation in the melting points of polyureas, polyamides, polyurethans, and polyesters with the length of the structural unit for compounds having units of 14-26 atoms. They give also a graph for the variation in the melting points of some polyesters of 1,10-decanediol, but some points are missing. Their data on polyamides are also incomplete. Moreover, Hill and Walker, in compiling their review article, have made use of results, which, being obtained by various workers under various conditions, frequently differ greatly from one another.

We have therefore undertaken the task of preparing a number of polyesters under identical conditions from a given diol and various dicarboxylic acids. With this object we have prepared polyesters of 1,20-eicosanediol and the dicarboxylic acids from oxalic to sebacic. In the case of oxalic and malonic acids, we used their esters—diethyl oxalate and diisopropyl malonate—as starting materials, because one of us with Rogozhin has shown that polyesters of sufficiently high molecular weight cannot be prepared from oxalic and malonic acids on account of the great tendencies of these acids to undergo thermal decomposition with evolution of carbon dioxide and formation of monocarboxylic acids [2]. The starting materials for the preparation of the other polyesters were 1,20-eicosanediol and the free dicarboxylic acids. The properties of the polyesters obtained are given in the table.

TABLE

Polyester	Formula	No. of C atoms		M. p. of polyester (°C)
		in acid	in unit	
Polyeicosamethylene oxalate . . .	$[-O(CH_2)_{20}OOC-CO-]_x$	2	24	88-90
Polyeicosamethylene malonate . .	$[-O(CH_2)_{20}OOC(CH_2)CO-]_x$	3	25	67-69
Polyeicosamethylene succinate . .	$[-O(CH_2)_{20}OOC(CH_2)_2CO-]_x$	4	26	86-89
Polyeicosamethylene glutarate . .	$[-O(CH_2)_{20}OOC(CH_2)_3CO-]_x$	5	27	77-80
Polyeicosamethylene adipate . . .	$[-O(CH_2)_{20}OOC(CH_2)_4CO-]_x$	6	28	85-87
Polyeicosamethylene pimelate . .	$[-O(CH_2)_{20}OOC(CH_2)_5CO-]_x$	7	29	82-84
Polyeicosamethylene suberate . .	$[-O(CH_2)_{20}OOC(CH_2)_6CO-]_x$	8	30	86-88
Polyeicosamethylene azelate . . .	$[-O(CH_2)_{20}OOC(CH_2)_7CO-]_x$	9	31	84-87
Polyeicosamethylene sebacate . .	$[-O(CH_2)_{20}OOC(CH_2)_8CO-]_x$	10	32	87-92

As will be seen from the results given in the table, the melting points of the polyesters obtained are dependent in a definite manner not only on the number of carbon atoms in the molecule of the acid, but also on whether this number is even or odd. Polyesters derived from dicarboxylic acids having even numbers of carbon atoms in their molecules have higher melting points than those derived from acids having odd numbers of carbon atoms, as will be particularly clear from Fig. 1, in which the relation between the melting point of the polyester of eicosanediol and the number of carbon atoms in the dicarboxylic acid molecule is represented graphically.

The dependence of the melting points of the polyesters on the number of carbon atoms in the acid is represented in Fig. 1 by a discontinuous curve, whereas the variation in the melting points of polyesters derived from acids having even numbers of carbon atoms is represented by a smooth curve (broken line in Fig. 1); another smooth curve (the second broken line in Fig. 1) represents the melting point variation for polyesters derived from acids having odd numbers of carbon atoms. The difference in form of these broken lines is worthy of note: it is to be related, of course, to the difference in the effect of increasing the number of carbon atoms in the two series of polyesters, derived from dicarboxylic acids having even and odd numbers of carbon atoms respectively.

We shall therefore make separate examinations of the effect of increasing the number of carbon atoms in the original dicarboxylic acid on the properties of eicosanediol polyesters of the "even series", of the same effect for the "odd series", and finally of the effect of passing from odd to even and back. Examination of Fig. 1 permits us to conclude that an increase of two in the number of carbon atoms in passing to the succeeding acid in the series of acids having even numbers of carbon atoms has no appreciable effect on the melting points of the polyesters, the individual steps being between 1° and 3°, and the total change from oxalic to sebacic acid being only 3°. Much greater changes occur in the polyesters derived from the "odd" acids: the change in the melting point from malonic to glutaric acid is 10°, from glutaric to pimelic 4°, and from pimelic to azelaic 3°, the total change from malonic to azelaic being 17°. Still greater changes are observed when we examine the whole series of these polyesters and compare even and odd compounds. The great change occurring in melting point when we pass from polyesters of even acids to polyesters of odd acids will be obvious; the former melt at higher temperatures than the latter.

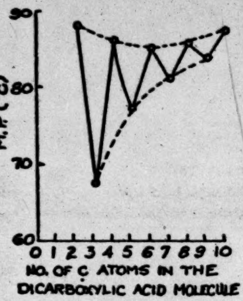

Fig. 1. Dependence of the melting points of eicosanediol polyesters on the number of carbon atoms in the acid component.

In order to determine the causes of the observed variations in the melting points of polyesters of eicosanediol, we must take into consideration the fact that polyethylene, which has a polymethylene chain, melts at 105°. All of the polyesters that we have prepared melt at lower temperatures, in spite of the low proportion of ester linkages in the molecule, which would lead us to expect a great similarity between these polyesters and polyethylene. This low melting point of the polyesters, in comparison with that of polyethylene, must evidently be associated with the increase in the flexibility of the polymer chain resulting from the introduction of oxygen linkages. Thus, polyethylene oxide [3] melts at 50-60°, and polydecamethylene oxide [4] at 58-60°. The increase in the flexibility of chains containing oxygen linkages is to be explained, as Aleksandrov and Lazurkin [5] have shown, in the following manner: the rotation of methylene groups around the bonds that unite them is not completely free owing to the resistance offered by the hydrogen atoms when they approach one another in the course of the rotation. The overcoming of this resistance requires an activation energy of 3000 cal/mole, whereas in the C−O−C linkage the activation energy is practically zero, there being no substituents on the oxygen to hinder free rotation around the C−O bond. For this reason the presence of C−O−C linkages in the chain increases its flexibility. These considerations are valid not only for polymers, but also for low-molecular-weight compounds, as can be seen from Fig. 2, in which curves are shown that indicate the changes in melting point in homologous series of alkanes, ethers, ketones, and carboxylic esters. Introduction of an ether linkage lowers the melting point, and the introduction of a carbonyl group raises it. Introduction of an ester linkage lowers the melting point, as can be seen from Fig. 2, in which the melting points in the homologous series of esters lie below those of the corresponding hydrocarbons. We may therefore conclude that, in the ester linkage C−O−CO−C, the effect of the ether linkage C−O−C predominates over that of the carbonyl group, resulting in the considerable lowering in melting point that we observe for the esters. As this relationship is valid for a large number of the members of homologous series of alkanes, ketones, ethers, and esters, it may clearly be extended to the class of polyesters, and in it we recognize the explanation of the results obtained in our investigation of the eicosanediol polyesters.

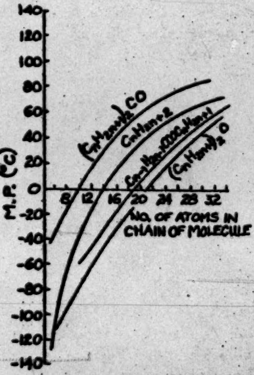

Fig. 2. Dependence of the melting points of ethers, esters, hydrocarbons and ketones on the number of atoms in the chain of the molecule.

In the series of polyesters derived from acids having odd numbers of carbon atoms, the melting points rise as the number of methylene groups in the acid increases; this is readily explained by the reduction in the concentration of ester groupings and the increase in that of the methylene groups, for as ester groupings cause a fall in the melting point, and methylene groups a rise, it is understandable that the general effect will be a rise in melting point. These considerations, however, cannot be applied to the series of polyesters derived from even acids, since we do not find here such a considerable variation in melting point as the number of methylene groups in the chain of the original acid is increased.

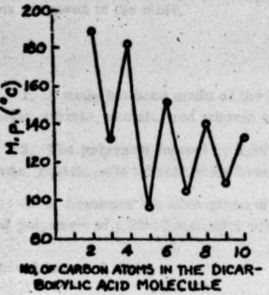

Fig. 3. Dependence of the melting point of a dicarboxylic acid on the number of carbon atoms in its molecule.

As we have already pointed out, comparison of polyesters derived from even and odd dicarboxylic acids reveals an obvious periodic variation in melting point: all polyesters derived from even acids melt higher than those derived from odd acids (see Fig. 1). If this behavior is compared with that of the dicarboxylic acids themselves, a considerable measure of resemblance between the courses of the curves will be noted (see Fig. 1 and Fig. 3).

As Nekrasov showed [6], the source of the periodic variation in the melting points and other physical properties in the homologous series of dicarboxylic acids lies in the differences in the configurations (cis-trans) of the even and odd dicarboxylic acids, which result, of course, in differences in the closeness of packing in the crystal and to differences in the strengths of the forces holding the molecules of dicarboxylic acid together in the crystal lattice; these, in their turn, find their expression in differences of melting point and other properties. Korshak and Rogozhin [2] have, for example, shown that the decarboxylation temperatures of dicarboxylic acids also vary in a periodic fashion, the odd dicarboxylic acids decomposing at lower temperatures than the even ones (see Fig.4).

The same factors, of course, preserve their significance also in the series of dicarboxylic acid polyesters, since they are determined by forces and causes of the same sort and order of magnitude. It may be considered that the main cause is the variation in the polarization of atoms in the acid molecule, which is determined by the variation in the distribution of charges. This must determine the closeness of packing and the strength of the forces binding the polyester macromolecules together — and therefore also the melting point, which is an expression of the strength of these forces.

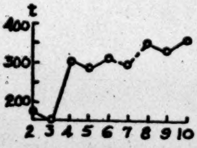

Fig. 4. Dependence of the dicarboxylation temperature of a dicarboxylic acid on the number of carbon atoms in its molecule.

EXPERIMENTAL

1,20-Eicosanediol

A 5% ethanolic solution of the diacetic acid of 1,20-eicosanediol, to which 5% on the weight of ester of hydrochloric acid had been added, was boiled under reflux for six hours in a round-bottomed flask. The reaction mixture was then transferred to a Favorsky flask, and ethyl acetate and excess of ethanol were distilled off. The residue was poured into a beaker and set aside overnight. The precipitate of eicosanediol was filtered off, washed several times with alcohol until the reaction to litmus was neutral, and air-dried. The eicosanediol was a white powder, melting at 101.5°; the literature gives m.p. 103° [7]. A 65-70% yield was obtained.

Polyeicosamethylene Sebacate

1,20-Eicosanediol (1.93 g) and sebacic acid (3 g) were placed in a condensation tube and heated in a bath of Wood's metal, constant temperature being maintained with the aid of a contact thermometer and a mercury relay. The reaction was at first carried out at 190° for 12 hours with continuous passage of nitrogen freed from oxygen; nitrogen was then excluded, and the system was connected to a vacuum pump, heating being continued at a pressure of 2-3 mm Hg at 210° for five hours. The temperature was then raised to 255°, and heating was continued under these conditions for a further 18 hours. The polyeicosamethylene sebacate was a white solid, readily dissolved when warmed with benzene, toluene, or xylene. When solutions in these solvents are cooled, the polymer is precipitated: from benzene solution at 28.5°, from toluene solution at 36°, and from xylene solution at 29.5°. In this respect polyeicosamethylene sebacate is very similar to polyethylene, which dissolves hot, and precipitates when the solutions cool. Polyeicosamethylene sebacate is soluble in cresol in the cold. It melts at 87-92°. Its specific viscosity (0.5% solution in cresol) is 0.176.

With the exception of the polyesters derived from oxalic and malonic acids, the remaining polyesters were prepared by the same method. The polyesters of oxalic and malonic acids were prepared by heating 1,20-eicosanediol with the ethyl or isopropyl esters of these acids taken in 150% excess. The properties of all of the polyesters are given in the table.

SUMMARY

1. A study has been made of the polycondensation of 1,20-eicosanediol with succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids and with esters of oxalic and malonic acids.

2. The polyesters formed by 1,20-eicosanediol with oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids have been prepared.

3. A discussion has been given of the causes of the differences observed in the melting points of the synthesized polyesters of 1,20-eicosanediol with dicarboxylic acids.

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* See Consultants Bureau Translation, page 509.

BRIEF COMMUNICATIONS

CERTAIN DERIVATIVES OF AMINOMETHYLPHOSPHONIC ACID

M. I. Kabachnik and T. Ya. Medved

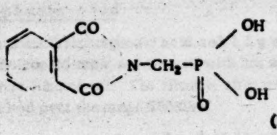
Aminomethylphosphonic acid, a phosphorus analog of glycine, has received very little study. Only a few methods for its preparation may be found in the literature [1, 2] and the best of these is the method that we have developed: the ammonolysis of diethyl chloromethylphosphonate [3]. We have described also the alkylation of aminomethylphosphonic acid with dimethyl sulfate, which resulted in the formation of the "phosphonobetaine" $(CH_3)_3\overset{+}{N}CH_2PO(OH)O^-$.

With the object of investigating the properties of aminomethylphosphonic acid and comparing them with those of glycine, we have carried out some acylation and alkylation reactions. It was found that aminomethylphosphonic acid is more difficult to acylate than glycine. Acetylation can be effected by heating aminophosphonic acid with excess of acetic anhydride in a water bath, when acetamidomethylphosphonic acid (I) is obtained in 57% yield.

$CH_3CONHCH_2PO(OH)_2$ (I) $ClCH_2CONHCH_2PO(OH)_2$ (II)

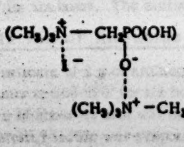
Fischer's method for the chloroacetylation of glycine in aqueous alkaline medium with chloroacetyl chloride [5] was found to be applicable to aminomethylphosphonic acid, but the yield was not good: (chloroacetamido)methylphosphonic acid (II), which was isolated as the aniline salt, was formed in 32% yield.

Fusion of aminomethylphosphonic acid with phthalic anhydride resulted in a 33% yield of the corresponding phthalimide derivative (III).



(III)

Interesting results were obtained when aminomethylphosphonic acid was alkylated with methyl iodide. When these substances were heated together in a sealed tube at 200-220°, unchanged aminomethylphosphonic acid was recovered from the reaction mixture. When, however, the reaction was carried out under the same conditions, but in a medium of methanol, an excellent yield was obtained of a quaternary iodide (IV) derived from the phosphonobetaine and containing two molecules of phosphonobetaine per iodide ion.



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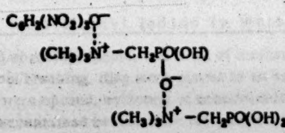

(V)

This iodide behaved as a tribasic acid when titrated with caustic soda in presence of phenolphthalein. When treated with moist silver oxide, it was quantitatively converted into the phosphonobetaine, m.p. 267°. An iodide of the same composition can be prepared from the free phosphonobetaine by the action of concentrated hydriodic acid, even when the latter is taken in great excess. It is evidently a general property of the phosphonobetaine to form salts of similar composition; thus we have previously [4] described a picrate of the phosphonobetaine that contained one molecule of picric acid for every two molecules of the phosphonobetaine (V).

In the methylation of aminomethylphosphonic acid with methyl iodide and methanol, a very small amount of methyl iodide is required: when reaction occurs in methanol at 200-220°, only 20% of the theoretically required amount of methyl iodide is sufficient to enable a 62% yield of the quaternary iodide to be obtained. This behavior must doubtless be attributed to re-formation, under the conditions of the reaction, of methyl iodide by reaction of methanol with hydriodic acid liberated during the methylation of the amino group. The methylation is brought about, in effect, by methanol, but in absence of methyl iodide it does not, of course proceed.

EXPERIMENTAL

Acetamidomethylphosphonic Acid

A mixture of 0.9 g of aminomethylphosphonic acid and 8 ml of acetic anhydride was heated in a boiling water bath for 2 hours 30 minutes. Excess of acetic anhydride was distilled off under reduced pressure, and the undistillable residue was treated with hot methanol. The solution obtained was concentrated, and when it had cooled down slightly yellowish crystals separated; they were recrystallized from methanol, yielding 0.7 g (57%) of product, m.p. 185°.

Found %: C 24.19; 24.05; H 5.19; 4.95; N 9.48; 9.57; P 20.26; 20.32
$C_3H_8NPO_4$. Calculated %: C 23.53 H 5.23 N 9.15 P 20.26

The substance titrated as a dibasic acid (against caustic soda with phenolphthalein as indicator). Equivalent weight: found 80.8, calculated 76.5.

(Chloroacetamido)methylphosphonic Acid

Aminomethylphosphonic acid (2.2 g) was dissolved in 19.7 ml of 2 N NaOH. The cooled solution was stirred, and chloroacetyl chloride (4.4 g) and 2 N NaOH (22.4 ml) were added alternately in small portions. An addition was then made of 6 ml of 5 N hydrochloric acid, and the liquid was evaporated down under reduced pressure at 30-35°. The residue, which was a white crystalline mass, was extracted several times with ethanol, and an alcoholic solution of aniline was added to the extract. The 1.2 g of white crystalline material that separated melted at 157°. The salt could be recrystallized from ethanol, but this treatment did not affect the melting point.

Found %: C 37.81; 38.42; H 5.17; 5.20; N 9.84; 10.17; P 11.44; 11.46
Cl 12.50; 12.46
$C_3H_7NO_4Cl \cdot C_6H_5NH_2$. Calculated %: C 38.50; H 4.99; N 9.98; P 11.05; Cl 12.66

Phthalimidomethylphosphonic Acid

A mixture of 1.1 g of aminomethylphosphonic acid and 1.5 g of phthalic anhydride was melted by being heated gently over a gauze. The cooled melt was treated with hot ethanol, and the undissolved crystals of unchanged aminomethylphosphonic acid were filtered off. The filtrate, after evaporation, yielded 0.8 g (33%) of a colorless crystalline substance, which melted over the range 280-285°.

Found %: C 45.12; 45.15; H 3.08; 2.74; H 5.50; 5.33; P 12.78; 12.95
$C_9H_8NPO_5$. Calculated %: C 44.80 H 3.30 N 5.80; P 12.86

Attempt to Methylate Aminomethylphosphonic Acid with Methyl Iodide

A mixture of 1 g of aminomethylphosphonic acid and 3 ml of methyl iodide was heated in a sealed tube at 200-220° for six hours. The aminomethylphosphonic acid was recovered unchanged from the reaction mixture.

Methylation of Aminomethylphosphonic Acid with Methyl Iodide in Methanol

A mixture of 2 g of aminomethylphosphonic acid, 6 ml of methyl iodide, and 6 ml of methanol was heated in sealed tubes at 200-220° for six hours (to prevent the tubes from breaking, they were placed in an autoclave in which a pressure of about 40 atm was established). When the tubes were opened, evidence of considerable pressure was noted. Methyl iodide was evaporated off, and the crystals that remained behind were recrystallized from methanol, yielding 3.2 g (82%) of a colorless crystalline substance, m.p. 220°.

Found %: C 21.90; 22.07; H 5.67; 5.55; N 6.45; 6.70; P 14.35; 14.40; I 29.47; 29.34

$C_8H_{25}N_2P_2O_6I$. Calculated %: C 22.12; H 5.76; N 6.45; P 14.30; I 29.26

Equivalent by iodine: found 435, calculated 434. Equivalent acidimetrically: found 145.8, calculated for a tribasic acid 144.7.

Methylation of Aminomethylphosphonic Acid with Insufficient Methyl Iodide in a Medium of Methanol

A mixture of 1 g of aminomethylphosphonic acid, 0.4 ml of methyl iodide (20% of the theoretically required amount), and 5 ml of methanol was heated in a sealed glass tube for six hours at 200-220°. The tube was opened, and the liquid was distilled, leaving 1.2 g (62%) of the iodide derived from the "phosphonobetaine" as residue.

The "Phosphonobetaine"

An aqueous solution of 2.7 g of the quaternary iodide of m.p. 220° was shaken with excess of freshly prepared moist silver oxide. Silver iodide and excess of silver oxide were filtered off, and the solution was treated with hydrogen sulfide. Precipitated silver sulfide was filtered off, and the filtrate was evaporated until a residue of constant weight was obtained. This was then recrystallized from absolute ethanol, yielding 1.35 g (87.0%) of the phosphonobetaine, m.p. 267°. A mixed melting point of this substance and the phosphonobetaine synthesized previously from aminomethylphosphonic acid and dimethyl sulfate showed no depression.

Found %: P 20.48; 20.38

$C_4H_{12}NPO_3$. Calculated %: P 20.26

Preparation of the Iodide Derived from the Phosphonobetaine from the Betaine and Excess of Hydriodic Acid

The phosphonobetaine (1 g) was dissolved in a small amount of water, and concentrated hydriodic acid (30 ml) was added to the resulting solution. The solution was evaporated down in a dish on a water bath, and the residue was dissolved in a small amount of water and reprecipitated with absolute ethanol, yielding 0.8 g of the iodide derived from the phosphonobetaine, m.p. 215°.

SUMMARY

1. Experiments on the acylation of aminomethylphosphonic acid show that it proceeds with greater difficulty than the acylation of glycine. Acetamidomethyl-, (chloroacetamido)methyl-, and phthalimidomethyl-phosphonic acids have been prepared.

2. The methylation of aminomethylphosphonic acid has been effected by means of methyl iodide in a methanol medium, and it has been shown that a quaternary iodide derived from the phosphonobetaine is formed. It has been established that methylation proceeds at the expense of methanol, so that much less than the stoichiometric amount of methyl iodide may be used.

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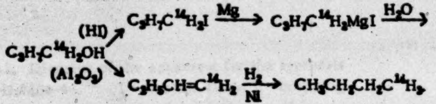
SYNTHESIS OF 1-BUTENE-4-C^{14} AND BUTANE-1-C^{14}

M. B. Neiman and G. I. Feklisov

The most widely used method for the introduction of radioactive carbon into the molecule of a hydrocarbon is the carbonation of alkylmagnesium halide complexes with radioactive carbon dioxide $C^{14}O_2$ [1]. 1-Butene-4-C^{14} and butane-1-C^{14} may, therefore, be synthesized according to the following schemes:

$$C_3H_7I \xrightarrow{Mg} C_3H_7MgI \xrightarrow{C^{14}O_2} C_3H_7C^{14}OOMgI \xrightarrow{H_2O} C_3H_7C^{14}OOH \xrightarrow{C_4H_9OH} C_3H_7C^{14}OOC_4H_9 \xrightarrow[250°;\ 400\ atm]{Cu\text{-}Cr} C_3H_7C^{14}H_2OH. \quad (1)$$



$$C_3H_7C^{14}H_2OH \xrightarrow{(HI)} C_3H_7C^{14}H_2I \xrightarrow{Mg} C_3H_7C^{14}H_2MgI \xrightarrow{H_2O} C_3H_7C^{14}H_3$$

$$C_3H_7C^{14}H_2OH \xrightarrow{(Al_2O_3)} C_2H_5CH{=}C^{14}H_2 \xrightarrow[Ni]{H_2} CH_3CH_2CH_2C^{14}H_3. \quad (2)$$

The synthesis of compounds labeled with radiocarbon by reactions similar to those in the first scheme has been carried out by Andreev and Andrianova [2].

In our laboratory we have prepared the labeled hydrocarbons propene-2-C^{14} [3], pentane-1-C^{14}, and pentane-3-C^{14} [4], and here we again used the method of carbonizing alkylmagnesium halide complexes with radioactive carbon dioxide. This method of preparing labeled hydrocarbons suffers, however, from a number of defects, e.g., the low yield of product and the large number of laborious operations.

The difficulties can be considerably lightened by the use of lithium aluminum hydride in the synthesis. A brief note has been published regarding a rational scheme for the preparation of 1-butene-4-C^{14} and butane-1-C^{14} [5]. The detailed working out of the synthesis of 1-butene-4-C^{14} and butane-1-C^{14} was performed by us with nonradioactive materials. The compounds were prepared in accordance with the following schemes:

$$BaC^{14}O_3 \xrightarrow{H_2SO_4} C^{14}O_2 \xrightarrow{LiAlH_4} C^{14}H_3OH \xrightarrow{PI_3} C^{14}H_3I \xrightarrow{Mg} C^{14}H_3MgI \xrightarrow{CH_2=CH-CH_2Br} C^{14}H_3CH_2CH{=}CH_2 \quad (3)$$

$$C^{14}H_3CH_2CH{=}CH_2 \xrightarrow[Ni]{H_2} C^{14}H_3CH_2CH_2CH_3. \quad (4)$$

Synthesis of 1-Butene-4-C^{14}. This was based on labeled methyl iodide prepared by the method that we have previously described [6]. Methylmagnesium iodide was prepared from 32 g of methyl iodide by reaction with magnesium in 50 ml of dibutyl ether, which had been previously dried over sodium and redistilled on a sand bath. The synthesis of butene was carried out in the apparatus shown diagrammatically in Fig. 1. The solution of methylmagnesium iodide in dibutyl ether was poured through a glass filter (to remove unchanged magnesium) into the reaction flask 1, which was heated in the water bath 6 to 70°. At this temperature, allyl bromide (30 g) was added dropwise from the funnel 2. The reaction of allyl bromide with methyl-C^{14}-magnesium iodide yielded 1-butene-4-C^{14} [7], which was collected in the trap 5, which was cooled with liquid nitrogen.

The 1-butene-4-C^{14} was purified by fractionation through a highly efficient low-temperature column. From 32 g of labeled methyl iodide, 7 g (55%) of 1-butene-4-C^{14} was obtained. In order to check the purity of the butene obtained, its vapor pressure was determined at a number of temperatures: the experimental points (Fig. 2) fall close to the vapor pressure curve for 1-butene, as constructed from data in the literature [8]. The butene obtained was subjected to combustion at 500° over copper oxide, and the carbon dioxide formed was converted into barium carbonate by treatment with baryta water. The radioactivity of the barium carbonate was determined with a surface counter, and the results are given in the table.

Synthesis of Labeled Butane. This was performed by the reduction of 1-butene-4-C^{14} with gaseous hydrogen over pyrophoric nickel. Into the autoclave 1 (Fig. 3) we placed 2 g of an alcoholic suspension of pyrophoric nickel and a sealed glass tube 3 which contained 5 g of 1-butene-4-C^{14} and had been cooled in liquid nitrogen. The air was pumped out of the autoclave, the valve was closed, and the electric furnace 2 was switched on so as to heat the tube of butene contained in the autoclave.

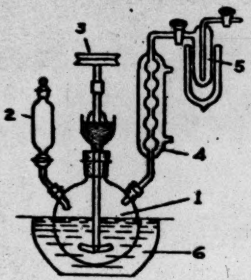


Fig. 1. Diagram of the apparatus for the synthesis of 1-butene-4-C^{14}: 1 – reaction flask; 2 – dropping funnel; 3 – stirrer; 4 – condenser; 5 – trap; 6 – water bath

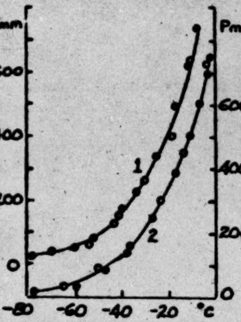


Fig. 2. Vapor pressure curves for butene (1) and butane (2): o – data from literature; o – experimental results (scale for butene on left; scale for butane on right)

At 80° the tube broke: the occurrence of this event was indicated by the reading of the manometer 4. In this was the autoclave was filled with butene. It was now cooled to room temperature and hydrogen was passed in from a cylinder until a pressure of 115 atm was attained. Agitation of the contents of the autoclave was effected by rotation of the latter by means of the electric motor 6. Hydrogenation of the butene proceeded to an extent of 85% in the first 30 minutes. When hydrogenation was complete, the butane formed was drawn from the autoclave with a pump and frozen with liquid nitrogen in the traps (8).

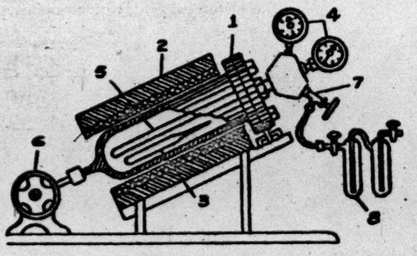


Fig. 3. Diagram of apparatus for the hydrogenation of butene to butane: 1 – autoclave; 2 – electric furnace; 3 – tube of butene; 4 – manometer; 5 – thermocouple; 6 – electric motor; 7 – valve; 8 – trap

The butane was purified by passage through wash bottles of bromine water and of concentrated sulfuric acid, and was then fractionated through a highly efficient column. From 5 g of 1-butene-4-C^{14}, 4.9 g of butane-1-C^{14} was obtained, the yield being, therefore, about 95%. The purity of the product was checked by determining its vapor pressure at various temperatures, and the results fitted satisfactorily to the curve constructed for butane from data in the literature [9]. By combustion of the butane-1-C^{14} and absorption of the $C^{14}O_2$ obtained in baryta water, the C^{14} present was converted into barium carbonate.

The results of the determinations of the specific activity of the butane-1-C^{14} obtained are given in the table. It will be seen from the table that the specific activities of both the butane-1-C^{14} and the 1-butene-4-C^{14} were practically identical with that of the starting material, $C^{14}H_3I$. Our comparisons of the activities of the three substances were, of course, based on figures relating to one active carbon atom.

TABLE

Relative Radioactivities of Synthesized 1-Butene-4-C^{14} and Butane-1-C^{14}

Compound	Weight of $BaC^{14}O_3$ precipitate (mg)	Calculated activity (imp./min)	Specific activity of $BaC^{14}O_3$ (imp·cm²/min·mg)	Specific activity of $BaC^{14}O_3$ per C atom
$C^{14}H_3I$	10.5	4346 ± 250	1500	1500
	11.7	4438 ± 250	1500	1500
$C^{14}H_3CH_2CH=CH_2$	23.8	1283 ± 70	370	1480
	20.8	1253 ± 70	370	1480
$C^{14}H_3CH_2CH_2CH_3$	15.6	1196 ± 70	370	1480
	17.4	1265 ± 70	370	1480
	15.6	1249 ± 70	370	1480

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